ATOMIC FLUORESCENCE FLAME SPECTROMETRY AS A MEANS OF CHEMICAL ANALYSIS

By

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I. INTRODUCTION

Atomic fluorescence flame spectrometry is a new method of chemical analysis. The principles on which the method is based have existed for several decades, but only recently has atomic fluorescence spectrometry been applied to chemical analysis. Because the technique is based on fluorescence emission by an atomic vapor excited by absorption of radiation, the flame was chosen as the best means of conversion of a solution sample into an atomic vapor and as a "container" for this vapor.

Factors which influence atomic emission and atomic absorption flame spectrometry also affect the results obtained by atomic fluorescence. In addition, the use of a light source poses several problems peculiar to fluorescence methods. In this investigation it was attempted to use atomic fluorescence flame spectrometry as a means of analysis as well as to measure several of the more common factors which apply to flame spectrometry. All sources which were available were used for excitation of the atomic vapor. Several types of flames were compared to determine the best choice for a given analysis. The use of aqueous and nonaqueous solvents, the addition of foreign gases to the fuel gas, and the choice of sheath gas surrounding the flame were also investigated. Comparisons of the results with existing flame spectrometric techniques were made to determine the value of the method for practical analyses.

The historical development of atomic fluorescence flame spectrometry was traced from the first experiments in atomic fluorescence in the early twentieth century to the present date. A brief discussion of the theory of atomic fluorescence flame spectrometry is given to provide a basis for understanding which factors would tend to influence the results to the greatest extent. Future instrumental improvements and applications are also discussed.

The elements zinc, cadmium, mercury, and thallium were found to fluoresce with high enough intensity that the method of atomic fluorescence flame spectrometry could be used for their analysis. This technique should be particularly suited to the routine determinations of mercury. Other elements should be added to this list as soon as suitable sources of excitation are available.

II. HISTORY

Mitchell and Zemansky (19) and Pringsheim (22) have discussed much of the original work on fluorescence of atomic vapors. In the last decade of the nineteenth century, the sodium D-lines were found to appear when sodium vapor was excited by sunlight or by a sodium flame. A band system of the Na_2 molecule (42) was also observed. A short time later Wiedemann and Schmidt (33), Wood (40, 41, 46), and Puccianti (23) failed to obtain the emission of the D-lines from sodium vapor excited by the D-lines. Wood (43, 46), however, observed the emission of the Na D-lines from a tube of sodium vapor excited by the D-lines from a sodium flame; the fluorescence radiation obtained consisted of only the D-lines themselves and showed a decrease in intensity for higher vapor pressures of sodium.

Wood (40, 41, 43, 46, 47, 48) and Dunoyer (9, 10, 11) thoroughly investigated the fluorescence of sodium vapor. Dunoyer obtained the fluorescence effect from a beam of fast-moving sodium atoms at the point of excitation. He showed that the resonance radiation was due to the atoms and that the time between the absorption and the subsequent emission of the light was quite short. He found that the resonance radiation was emitted only from the point where the exciting radiation crossed the atomic beam, and little or no spreading of the resonance radiation occurred in the direction of motion of the atoms. Dunoyer showed that only the center of the D-line is useful for producing fluorescence. Sources with reversed lines gave a decrease in the amount of fluorescence obtained.

Bogros (5) obtained fluorescence of an atomic beam of lithium by illumination with the radiation of a lithium flame. In 1912 Wood (44, 45) obtained only the 2537 A. line in the fluorescence of mercury vapor because the quartz mercury arc used gave only the unreversed line at 2537 A. Terenin (31, 32) obtained the fluorescence of cadmium vapor (the 2288 A. and 3261 A. lines) by using a vacuum arc in cadmium. The 2288 A. or the 3261 A. fluorescence line was excited by a source giving radiation of a wavelength the same as that observed in fluorescence. Filters were used to eliminate all but the desired excitation source line. Zinc fluorescence was obtained (21, 28, 34) by excitation of zinc vapor.

Many atoms have energy levels of magnitude such that they will exhibit both resonance radiation and line fluorescence. An atom may absorb a line from the source, being raised to an excited energy level; then it may return to the lowest state, emitting resonance radiation, or may drop to a low-lying metastable state, giving line fluorescence. The fluorescence of thallium, initially investigated by Terenin (31, 32), is an example. Absorption of the 3776 A. line can give either the 3776 A. or 5350 A. lines as fluorescence. The 3776 A. line is the resonance line, and the 5350 A. line is due to a transition to the metastable $6^2P_{3/2}$ state. Similarly the 2768 A. thallium line can give rise to both the 2768 A. and 3530 A. lines. Terenin also investigated the fluorescence of lead, bismuth, arsenic, and antimony (31, 32).

Strutt (29, 30) and later Christensen and Rollefson (6) excited sodium vapor with the 3303 A. doublet from a vacuum arc in sodium and obtained the 3303 A. doublet and the D-lines in the fluorescence. A step-like process was proposed such that the absorption of the radiation of the 3303 A. lines raises the atom to the $4^2P_{1/2,3/2}$ states. Strutt obtained resonance line fluorescence (Na D-lines) as a result of 3303 A. absorption. The mechanism of deactivation of the excited sodium atom could be described by either of the two processes below.

$$\text{(I)}\quad 4^2P \longrightarrow 4^2S \longrightarrow 3^2P \longrightarrow 3^2S$$

$$\text{(II)}\quad 4^2P \longrightarrow 3^2D \longrightarrow 3^2P \longrightarrow 3^2S$$

The latter step in each gives rise to the D-lines, and the first two steps give emission in the infra-red region. Strutt (30) also examined the breadth of the resonance D-lines and found agreement with his predictions based on the Doppler effect. Wood and Dunoyer (47) found that excitation with only one D-line gave only that line as fluorescence. Wood and Mohler (48, 49) later showed that this is true only for pure sodium vapor. The presence of foreign gases results in energy transfer to the other D-line.

Fuchtbauer (14) was the first to investigate the absorption of radiation by excited atoms and their subsequent fluorescence. In his work on mercury vapor, he showed that after the necessary excitation by absorption of the 2537 A. line and subsequently other lines of longer wavelength, considerable fluorescence was observed. Absorption of the 2537 A. line and subsequent absorption of the 3131.5 A. and 3125 A. lines will give the 5770 A., 3654 A., 3131.5 A., and 3125 A. lines as fluorescence in addition to the resonance radiation. Absorption of the 3131.8 A. line by atoms excited by the 2537 A. line will give the 2967.5 A., 3131.8 A., and 3663.2 A. lines with the 2537 A. line. Bender (3) obtained similar effects for cadmium and zinc.

Fluorescence of species in flames was first reported by Nichols and Howes (20) as a result of their work on photoluminescence of flames. They obtained slight increases in the emission of calcium, strontium, barium, lithium, and sodium by excitation of the flame supplied with these elements with various sources, none of which contained any appreciable amount of the element excited. A thallium flame excited with a mercury arc containing thallium showed an increase in intensity of 7%. This increase was ascribed to the effect of the thallium lines of the source. Badger (2) thoroughly investigated flame fluorescence for a wide variety of elements and noted the slight effect of the flame itself on fluorescence.

At a more recent date Robinson (26) observed a small amount of fluorescence of the Mg 2852 A. line when an oxy-hydrogen flame into which was atomized a 1000 p.p.m. solution of magnesium was excited by a magnesium hollow cathode discharge tube. Under similar conditions he did not observe fluorescence from the Na 5890 A. line, the Ni 3524.5 A. line, or the Ni 3414 A. line.

At the International Spectroscopy Colloquium in 1962 Alkemade (1) told of the use of atomic fluorescence of flames as a means of determining quantum yields and referred to its possible use as a means of analysis. He briefly compared atomic fluorescence and atomic absorption flame photometry and described the experimental setup used to measure the quantum efficiency of the Na 5890 A. line with respect to flame gas composition. Earlier Boers, Alkemade, and Smit (4) had used this method for the measurement of the quantum efficiency of the Na 5890 A. line for sodium vapor in a propane-air flame.

III. THEORY

The theory of atomic fluorescence flame spectrometry has been discussed by Winefordner and Vickers (39). Atomic fluorescence flame spectrometry is based on the absorption of radiation of a particular wavelength by atoms in the vapor state and their subsequent deactivation by emission of radiation of the same or longer wavelength. Both the absorbed and emitted wavelengths are characteristic of the atoms which are undergoing the transitions.

In the case of atomic emission flame spectrometry the atoms are excited thermally and the emission is measured. For atomic absorption flame spectrometry the decrease in intensity of the characteristic radiation from a source due to absorption by the atomic vapor in the flame is the measured quantity. Atomic fluorescence flame spectrometry measures the emission resulting from atoms excited by means of absorption of radiation. Of course, any thermal emission present must be subtracted from the total emission measured.

Atomic fluorescence may be divided into four types (39) according to the manner of excitation and emission. Resonance fluorescence refers to absorption and emission at the same wavelength. Absorption of resonance radiation and emission due to a radiational transition to a metastable state is called direct line fluorescence. Stepwise line fluorescence occurs when the atom is raised to an excited level by absorption of resonance radiation and then emits radiation at some longer wavelength. The fluorescence emission arises from these radiational deactivations to the ground state. Sensitized line fluorescence refers to collisional activation of an atom by a foreign atom which has been activated by absorption of its characteristic resonance radiation.

The intensity of the fluorescence emitted radiation should depend on the amount of exciting radiation absorbed, on the conversion efficiency of absorbed to emitted radiation, on the amount of emitted radiation absorbed by ground state atoms, and on the intensity of the excitation source. The fluorescence intensity, I_F, for resonance fluorescence is given (39) by equation 1,

$$I_F = \frac{\phi P^{\circ} \Delta\nu}{4\pi A_f} (1-e^{-k^{\circ}L})e^{-k^{\circ}L/2}\cosh(k^{\circ}L/2) \quad \text{watts/cm.}^2\text{-ster.,} \quad (\underline{1})$$

where ϕ is the quantum efficiency accounting for loss of energy by processes other than fluorescence; P° is the incident radiant power, in watts, per unit frequency interval, in sec.$^{-1}$; $\Delta\nu$ is the half the base width of the triangle whose area represents the total power absorbed by the line, in sec.$^{-1}$; A_f is the area of the flame, in cm.^{2}; k° is the atomic absorption coefficient at the line center, in cm.$^{-1}$; and L is the average path length of the radiation through the flame, in cm.

The atomic absorption coefficient at the line center, k°, is directly proportional to $N_\circ$, the ground state concentration of the absorbing atoms, in atoms/cm.^{3} of flame gases. Thus for a given element in an invariant flame sample cell the fluorescence intensity, I_F, should be directly proportional to the incident radiant power, P°. Variations in flame conditions would affect I_F primarily through changes in L, A_f, and ϕ within a small flame temperature range. Using a constant excitation source a plot of I_F against $N_\circ$, or concentration, should be linear. At higher concentrations the linearity should disappear since with increasing $N_\circ$ the term $(1-e^{-k^\circ L})$ approaches unity and $e^{-k^\circ L/2}$ approaches zero, causing the curve to go through a maximum and then decrease. At sufficiently high values of $N_\circ$ the quantum efficiency, ϕ, may decrease due to self-quenching (19, 22).

A typical experimental arrangement (39) shown in Figure 1 for atomic fluorescence flame spectrometry would consist of an intense, unreversed source of radiation which is focused on a flame containing an atomic vapor of the element being investigated. At right angles to the beam of radiation from the source to the flame, the optical axis of the monochromator is aligned in such a manner that the two axes intersect at the flame cell. At the exit slit of the monochromator a photomultiplier tube detector is mounted and connected to a sensitive amplifier. The amplified signal is then fed to either a meter or a recorder.

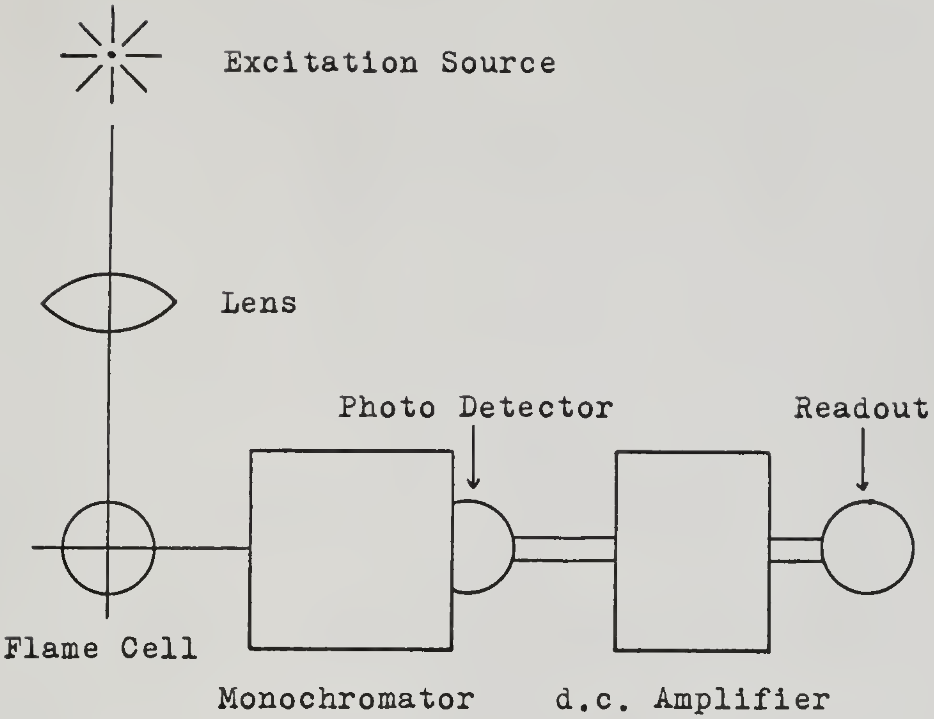

Figure 1. Block Diagram of Experimental Setup for Atomic Fluorescence Flame Spectrometry

Any source emitting radiation at the wavelength required may be used providing it is intense and not reversed. However, a very wide line source will result in a decreased fluorescence signal compared to a narrow line source of the same intensity because absorption occurs only over the width of the absorption line. A continuum source could be used for excitation if it were sufficiently intense over the width of the absorption line and if a monochromator of small spectral band width were used to decrease the scattering signal.

When fluorescence is measured at the same wavelength as that used for excitation, scattering of the source radiation is usually the main factor in determining the limit of detection. In cases where the fluorescence is measured at a wavelength longer than that used for excitation, scattering can be eliminated by use of a monochromator or narrow band filter.

Atomizer-burners useful for atomic emission and atomic absorption flame spectrometry are also useful for atomic fluorescence. The total-consumption type is common and easy to use but has the disadvantages of having a small flame size and of giving light scattering due to unevaporated solvent droplets. Chamber-type atomizers have less scattering problems due to smaller droplets being introduced into the flame and do provide a flame cell of greater size, but they have the disadvantages of being cumbersome as well as extremely wasteful of sample solution. In addition, the chamber-type atomizers are used with low temperature flames which results in incomplete compound dissociation in many cases.

Any monochromator which is useful for atomic emission can be used for atomic fluorescence measurements if its range includes the ultraviolet. Better sensitivity might be expected, however, from instruments with better dispersion and better entrance slits and optics. Below 3000 A. a sensitive d.c. amplifier can be used because thermal emission is low, but above this wavelength an a.c. amplifier tuned to the frequency of a chopper in the beam of the exciting radiation should give the best results. Photomultiplier tube detectors and meter or recorder readout systems would be the same in either case.

IV. EXPERIMENTAL CONSIDERATIONS

A. Apparatus

The experimental components were arranged as described in the previous section on the theory of atomic fluorescence flame spectrometry. All components, individually described below, when using total-consumption atomizer-burners, were held in place by means of two triangular optical benches (one 0.5 meter long, No. 22-702, and one 1.0 meter long, No. 22-704, The Ealing Corp., Cambridge 38, Mass.), which were mounted with the shorter bench perpendicular to the longer bench at its midpoint on a piece of 0.5 inch thick Bakelite. All components were fastened to the optical benches with 13.5 mm. diameter rods which were held in carriers (No. 22-728, The Ealing Corp.). These carriers could be positioned at any point on the optical benches. The monochromator-detector combination and the burner were mounted on the longer optical bench, and the excitation source was mounted on the shorter optical bench. Figure 1 illustrates the relative placement of the components.

In the cases where the Meker burner was used the monochromator-detector assembly was mounted on blocks, because the additional height made necessary by the taller burner was not obtainable with the optical bench and carrier arrangement. The burner and source were then mounted on weighted-base ringstands and secured with universal laboratory clamps.

Since most of the elements considered were extremely toxic (27), a hood made from a 3.5 x 7 x 7 inch box open at the bottom and fitted with 1.75 inch diameter flexible plastic-jacketed steel tubing at the top was positioned over the flame. This tube was connected to the intake of a centrifugal blower, and the vapors were carried from the blower by similar tubing to a laboratory hood.

Sources. Zinc and cadmium Osram spectral lamps (The Ealing Corp.) with one-inch diameter holes cut in their outer soft glass envelopes to allow unobstructed passage of light from the quartz inner bulb were operated on a.c. at the recommended current of 1.5 amperes using a step-up transformer and ballast. The holes in the Osram lamps were made by carefully heating the desired portion of soft glass by means of an oxyacetylene flame and allowing the inner vacuum to draw in the softened glass. The inverted glass shell, which was quite thin, was then cracked and the edges firepolished. The lamps were mounted in a medium prefocus socket (No. 26-250, The Ealing Corp.) containing a mounting pin in the center of its base for positioning in a carrier.

For mercury a Hanovia mercury vapor lamp (No. 90012, Hanovia Chemical and Mfg. Co., Newark 5, N. J.) operated with a reactive transformer (No. 23634, Hanovia Chemical and Mfg. Co.), a Hg-S Osram spectral lamp (The Ealing Corp.)

operated at 1.1 amperes, a Philips Hg spectral lamp (The Ealing Corp.) run at 0.9 ampere, and a mercury electrodeless discharge tube were used. The mercury electrodeless discharge tube (Ophthos Instrument Co., Rockville, Md.) was held at one end by a thermometer clamp (No. S-19427, E. H. Sargent and Co., Chicago 36, Ill.) in the center of a 2450 mc. resonant cavity (Ophthos Instrument Co.) having an observation port. Power was supplied to the cavity by a coaxial cable (No. 73624G2B, Raytheon Co., Waltham 54, Mass.) from a 100 watt microwave power generator (Model PGM-10X1, Raytheon Co.). The resonant cavity and the Hanovia mercury lamp were held in place by means of universal laboratory clamps. The Hg-S Osram lamp was mounted the same as the zinc and cadmium Osram lamps, and the Philips lamp was placed in a standard candelabra screw-base socket equipped with a mounting pin for placement in a carrier.

In the case of thallium both the Osram lamp and the electrodeless lamp were used. The Osram lamp (The Ealing Corp.) was operated, as mentioned above, at 1.0 ampere and the electrodeless lamp (Ophthos Instrument Co.) also was operated as above. Electrodeless lamps (Ophthos Instrument Co.) were also used for gallium, indium, antimony, and selenium.

When using the electrodeless lamps or the Hanovia mercury vapor lamp, the radiation was focused on the flame by means of a 5.0 mm. focal length quartz lens. This lens was mounted in a holder (No. 22-810, The Ealing Corp.) and then fixed in a carrier and positioned on the 0.5 meter optical bench. For the Osram and Philips spectral lamps no lenses were used. The lamps were moved as close to the flame as possible. However, in this case it was necessary to shield the entrance slit of the monochromator from the incident source radiation by placing flat black baffles along the sides of the lamp.

In some cases air cooling of the electrodeless discharge tubes was necessary. This was done by mounting a small centrifugal blower below the resonant cavity so that it would force a current of air through the center passage of the cavity and over the discharge tube.

Atomizer-Burner. Beckman medium-bore total-consumption atomizer-burners (Nos. 4020 and 4030, Beckman Instruments, Inc., Fullerton, Calif.) and a Meker burner (No. 3-902, Fisher Scientific Co., Pittsburgh 19, Pa.) fitted with a chamber atomizer were used for all studies. The Beckman burner was mounted on a rod (6 inches long by 13.5 mm. diameter) and held in a carrier on the optical bench. Under the atomizer capillary a small piece of aluminum sheet was positioned to hold the sample cuvettes and was mounted on a swivel so that it could be moved out from under the capillary. The oxyacetylene burner was used for both oxyacetylene and air-hydrogen flames, while the oxyhydrogen burner was used only for oxyhydrogen flames. The latter burner was also fitted with a sheath attachment

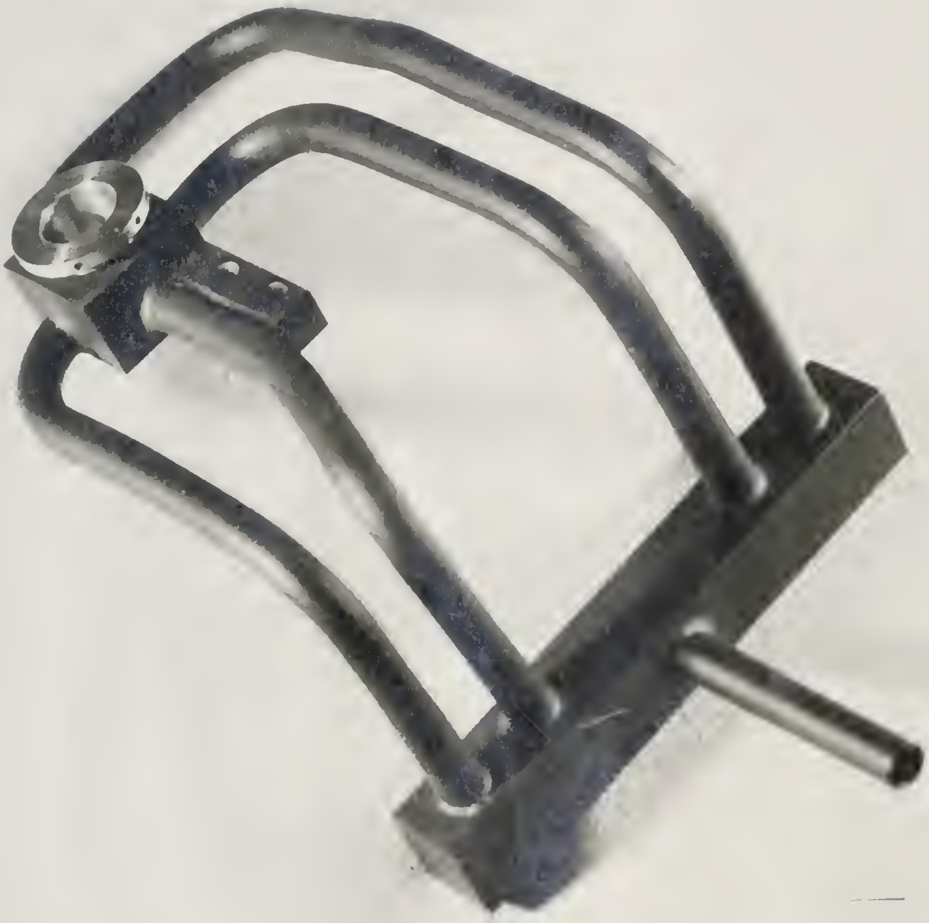

Figure 2. Beckman Custom Sheath Attachment

(Custom made, Beckman Instruments, Inc.), shown in Figure 2, for determining the effect of sheath gases on fluorescence.

The Meker burner, used with natural gas and air, was modified by sealing the air ports at the base of the burner tube, drilling at right angles into the gas fitting and mounting a stainless steel tube in the hole so that fuel, air and atomized sample might be premixed. A Beckman small-bore total-consumption atomizer-burner (No. 4050, Beckman Instruments, Inc.) and a short piece of glass tubing equipped with a length of rubber tubing and a pinchclamp were inserted in a two-hole rubber stopper which was placed in the lower end of a five-inch long and one-inch diameter glass tube. The upper end of this tube was closed with a one-hole rubber stopper holding a piece of glass tubing bent at a right angle; this glass tubing and the stainless steel tube added to the Meker burner were joined with a short length of rubber tubing. The Meker burner and chamber atomizer are shown in Figure 3.

Acetylene, hydrogen, oxygen, and air were regulated by pressure reduction valves on the standard gas cylinders and by a Beckman control panel (No. 9220, Beckman Instruments, Inc.). The flow rates of all gases were measured by means of rotameters (No. 4-15-2, Ace Glass Inc., Vineland, N. J.) placed in the gas lines between the regulators and the burner. Air for the Meker burner was regulated using the above system, and the natural gas was measured

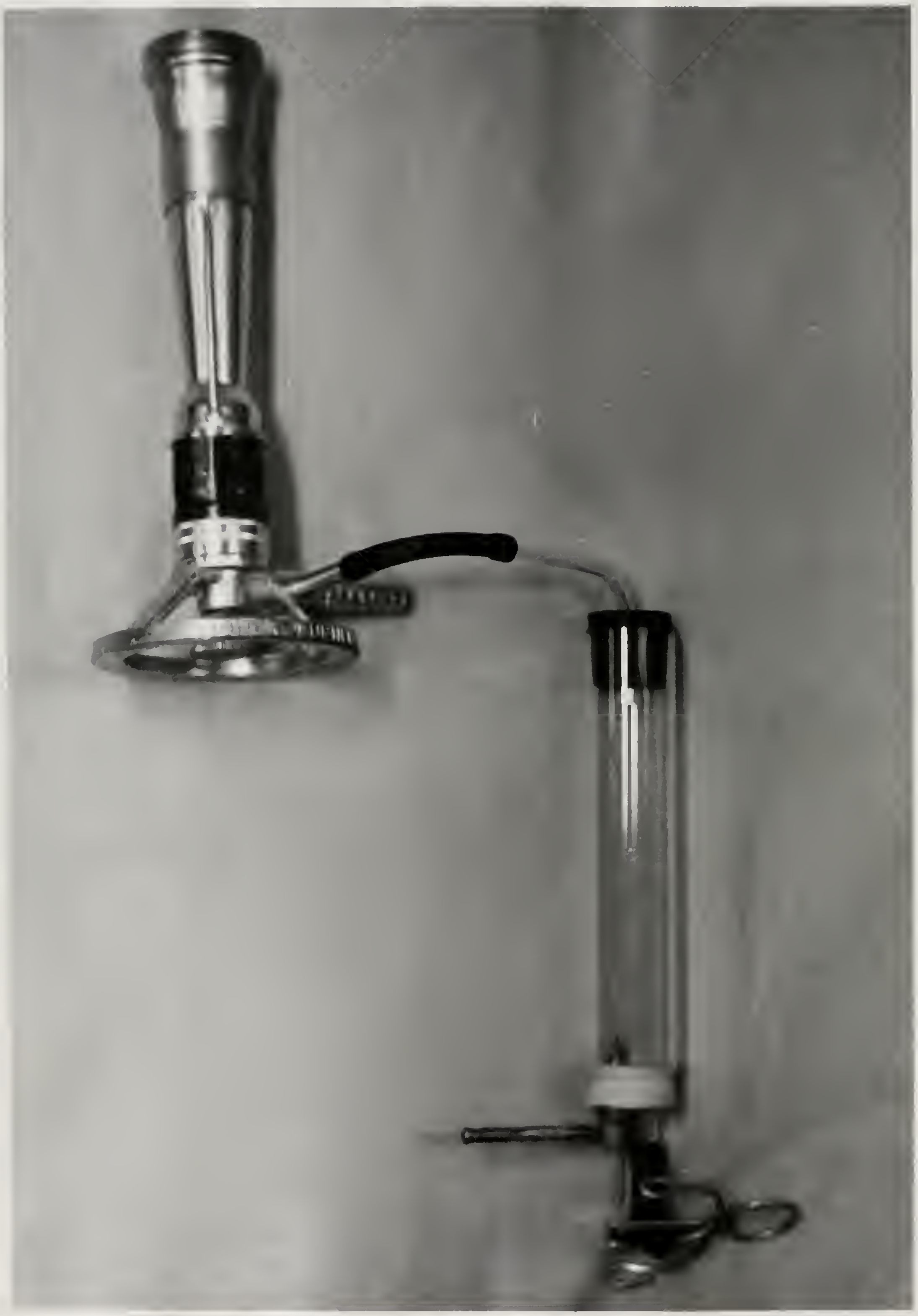

Figure 3. Chamber Atomizer Fitted to the Modified Meker Burner

by means of a rotameter and controlled by the gas jet tap on the laboratory bench. Provision was made to add gases to the sheath attachment or to the fuel gas just before it entered the burner by means of a "Y" tube in the fuel gas line. The sheath gases were controlled by pressure reduction valves and needle valves on the gas cylinders, and separate rotameters were used to determine gas flow rates.

Monochromator-Detector. A small, inexpensive Bausch and Lomb grating monochromator (No. 33-86-25, Bausch and Lomb Optical Co., Rochester 2, N. Y.) with UV grating (No. 33-86-01, Bausch and Lomb Optical Co.), visible grating (No. 33-86-02, Bausch and Lomb Optical Co.), and variable slits (No. 33-86-31, Bausch and Lomb Optical Co.) was used for all studies in this research. A 5 mm. horizontal slit made from a piece of 1/16 inch aluminum was placed in front of the entrance slit of the monochromator in order to limit the height of the flame affecting the detector. Two pins (3 inches long and 13.5 mm. diameter) were mounted on a 1/8 inch aluminum plate (5 x 8 inches) on the same axis as the slits of the monochromator; the monochromator was screwed to the plate. These pins were placed in carriers which were used to position the monochromator on the one-meter optical bench. An upright detector housing (No. 2000316, Eldorado Electronics Co., Berkeley, Calif.) containing an RCA 1P28 photomultiplier tube was placed at the exit slit of the monochromator and held in place by a light tight sleeve. A high gain, high stability d.c. amplifier with meter readout and with a 10 mv. recorder output (Model ph-200, Eldorado Electronics Co.) was connected to the photomultiplier tube and used for amplifying and displaying the input signal. Measurements were taken on either a 10 mv. recorder (G-11A, Varian Associates, Palo Alto, Calif.) or a 12.5 mv. recorder (Model-SR, E. H. Sargent and Co.).

Atomic Absorption. Atomic absorption measurements were taken using the same components as used for atomic fluorescence, except that the source and flame were then optically aligned with the monochromator. The source and lens were placed so as to focus the source radiation on the center of the flame at the desired position above the burner tip. The transmitted radiation was then focused by means of a second lens on the entrance slit of the monochromator.

B. Solutions

Stock solutions containing 1000 p.p.m. of the elements being investigated were prepared as described below. All other solutions were prepared by successive dilutions. Zinc, cadmium, and mercury solutions in 0.01 M HCl were prepared from $ZnCl_2$, $CdCl_2$, and $HgCl_2$, respectively. Thallium and indium solutions were made acidic and were prepared from $TlNO_3$ and $In(NO_3)_3 \cdot 3H_2O$. Antimony, gallium, and selenium solutions were prepared from the metal by dissolving in acid and diluting to volume. Solutions of the elements in 30% and 70% methanol in water solutions were prepared by pipeting 10 ml. of the 1000 p.p.m. stock aqueous solution into a 100 ml. volumetric flask, adding the necessary volume of pure methanol to reach the proper methanol to water ratio and then diluting to 100 ml. with the respective methanol-water solvent system.

C. Procedure

The metal vapor lamp was optically aligned to give maximum intensity of source radiation on the flame with a minimum amount of light reflected into the monochromator. The lamp was turned on, and the current was adjusted to the desired value. In the case of the electrodeless discharge lamps the generator power was set as desired, and the cooling blower was started if needed. The electrodeless lamps were started by turning the microwave generator to full power and igniting by means of a Tesla coil. This was done by inserting a two-inch glass tube with a wire trimmed flush with the open end into the resonant cavity observation port. The wire was an extension of the Tesla coil electrode. The voltage of the Tesla coil was then slowly increased until the lamp started. In several cases it was necessary to vaporize the compound in the lamp by heating the lamp in the flame of a Meker burner to facilitate starting of the lamp. The lamps were run under the conditions listed in Table 1.

Table 1

Operating Conditions for
Atomic Fluorescence Excitation Sources

Type Lamp	Element	Conditions
Osram spectral	Zn	1.5 amperes
	Cd	1.5 amperes
	Hg	1.1 amperes
	Tl	1.0 ampere
Philips spectral	Hg	0.9 ampere
Hanovia vapor discharge	Hg	non-adjustable
Ophthos electrodeless discharge	Hg	40% power, air cooled
	Tl	40% power, no cooling
	Ga	60% power, air cooled
	In	50% power, no cooling
	Sb	70% power, no cooling
	Se	60% power, no cooling

These values were obtained from either manufacturer's recommendations or by measurement to determine maximum intensity without having line reversal or losing stability. The lamps usually were allowed about 15 minutes to stabilize. Long term stability of the lamps resulted in negligible error as did the lamp flicker (approximately 2% peak-to-peak). While the lamp was warming up, the amplifier circuit and photomultiplier high voltage power supply were turned on and were allowed to warm up.

The monochromator was set to the wavelength being measured by introducing a concentrated solution (1000 p.p.m.) of the metal being analyzed into the flame and adjusting the wavelength dial to obtain a maximum fluorescence signal. The wavelengths chosen for the elements investigated are given in Table 2.

Table 2

Wavelengths Used for Measurement of Atomic Flame Fluorescence

Element	Wavelength, A.
Zn	2137
Cd	2288
Hg	2537
Ga	4033, 4172
In	4102, 4511
Tl	3776
Sb	2068, 2529, 2598, etc.
Se	2040, 2591

For several reasons which will be discussed later, fluorescence was not observed in the cases of gallium, indium, antimony, and selenium. These elements will be omitted from further discussion of experimental conditions.

Before a series of standard solutions could be run for obtaining a working curve and determining the limit of detection, the position of excitation and measurement of fluorescence in the flame, the slit width of the monochromator, and the flame gas composition had to be optimized. The position of the fluorescence in the flame was determined by varying the burner height with respect to the entrance slit of the monochromator while the excitation source and the entrance slit of the monochromator were kept at the same level. For zinc and cadmium the best position in the flame was halfway between the tip of the reaction zone and the tip of the outer cone of the flame. These positions are illustrated in Figure 4a. In the case of the Meker burner all measurements were taken midway between the reaction zone and the tip of the outer cone of the flame as shown in Figure 4b. The optimum slit width was chosen such that the signal-to-noise ratio (the signal due to fluorescence-to-the-flicker in the background, which was a result of random scattering of incident radiation, flicker in the excitation source, and flicker in the flame continuum) was a maximum without giving readings impossible to measure with a reasonable degree of accuracy

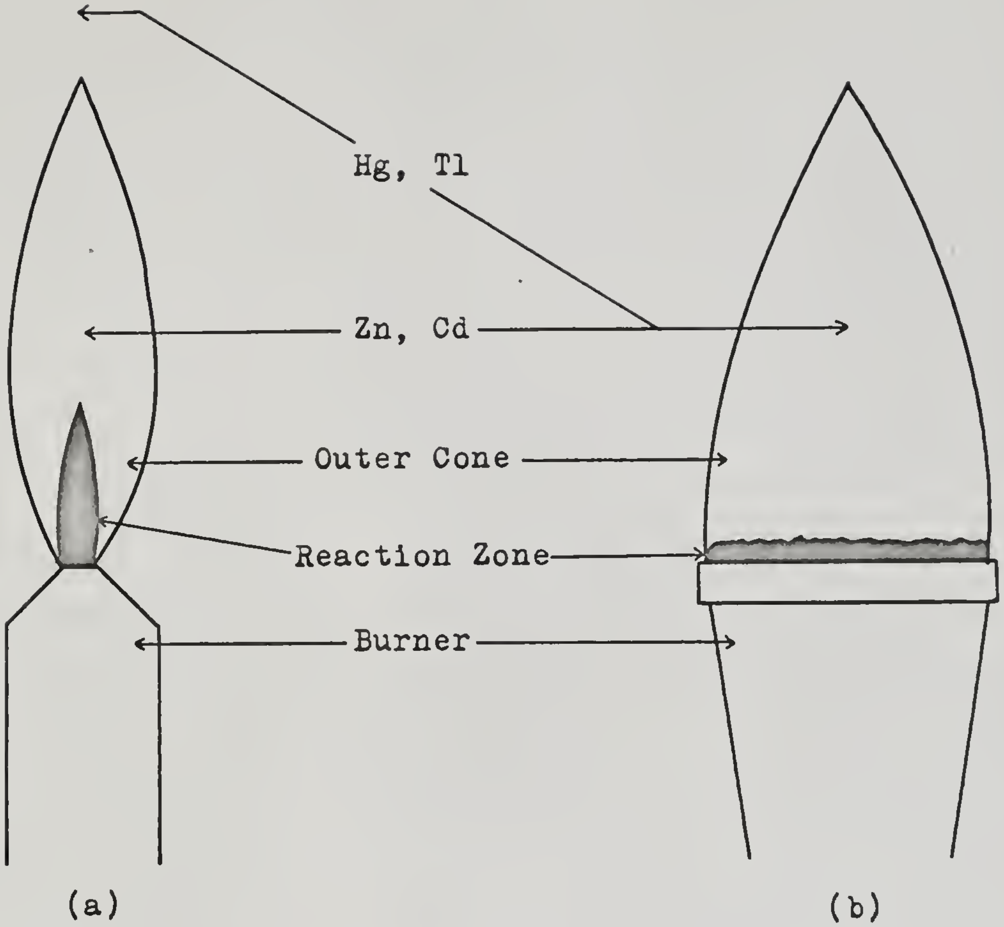

Figure 4. Position of Excitation and Measurement of Atomic Fluorescence with the (a) Beckman Total-Consumption Atomizer-Burner Flame and with the (b) Meker Burner Flame

when operating near the limit of detection, i.e., at high amplifier sensitivities. The exit slit was set to 0.56 of the value of the entrance slit for optimum spectral resolution. Entrance slit widths for the Meker burner were all found to be 0.50 mm., and for the total-consumption atomizer-burner they were 0.25 mm., 0.20 mm., 0.40 mm., and 0.25 mm. respectively for zinc, cadmium, mercury, and thallium.

Flame gas composition was chosen by measuring the signal-to-noise ratio for a variety of flame compositions and choosing the value which maximized the ratio. In all cases where the Beckman burner was used, the oxygen or air flow rate was fixed at 2500 cc./min. in order to hold the solution flow rate constant for all measurements. The flow rates of the fuel gases are given in Table 3. In all cases for the Meker burner, the air flow rate was 2800 cc./min. and that of the natural gas was 4000 cc./min.

The relative intensity due to the atomic fluorescence of a particular line was obtained as follows. The sample solution was introduced into the appropriate flame, and the sensitivity multiplier of the amplifier was adjusted to bring the reading into the range of the meter. Then the solvent being used was introduced and a background reading was taken at the same instrument setting. The relative fluorescence intensity was obtained by subtracting the background signal (due to incident light scattering by solvent droplets in the flame and to the emission of background radiation by the flame gases) from the signal due to the sample. As the concentration of the samples introduced changed, the gain of the amplifier was increased or decreased in known increments, and measurements were obtained over a wide concentration range.

Table 3

Fuel Gas Flow Rates for Various Elements and Flames When Using Beckman Total-Consumption Atomizer-Burners

Element	Flame	Fuel flow rate, cc./min.
Zn	H_2/air	8000
	H_2/O_2	5000
	C_2H_2/O_2	1000
Cd	H_2/air	8000
	H_2/O_2	5000
	C_2H_2/O_2	1000
Hg	H_2/air	10000
	H_2/O_2	8000
	C_2H_2/O_2	1200
Tl	H_2/air	8000
	H_2/O_2	8000
	C_2H_2/O_2	1200

If the sample also emitted thermally, then an additional reading of thermal emission had to be made by blocking off the source radiation and measuring the thermal emission of the sample and the background due to the solvent and taking the difference of the two values. This reading for thermal emission was then subtracted from the reading made for atomic fluorescence, because in this case it was actually a reading of both fluorescence and emission. However, in the four instances where fluorescence was observed, only the Tl 3776 A. line exhibited measureable emission for concentrations below 1000 p.p.m. using the experimental setup described.

For a given element each series of readings using the same flame was normalized to correct for small experimental variations from day to day so that an accurate comparison might be made. The normalizing procedure consisted of first measuring the intensity of a specific standard solution, i.e., 10 or 100 p.p.m. aqueous solution, as a control and then measuring the fluorescence signal of the system under investigation. All control readings for the same conditions were averaged. A normalizing factor for the measurements made under these conditions was computed by dividing the average control reading by the specific control reading for that series. All measurements in a series were then multiplied by the normalizing factor calculated from the control reading for that series.

The effect of argon, nitrogen, and oxygen as sheath gases was investigated for zinc and mercury in the oxyhydrogen flame. The flow rates of each gas added to the sheath was 1000 cc./min. Measurements of relative fluorescence intensity were made for 10 p.p.m. aqueous solutions of the elements being investigated.

Addition of foreign gases to the flame by premixing argon or nitrogen with the fuel gas was studied for zinc, cadmium, mercury, and thallium in both oxyhydrogen and oxyacetylene flames. The flow rate of the fuel gas was the same as when no foreign gas was added and the flow rates of argon and nitrogen were 870 cc./min. and 1000 cc./min., respectively. Solutions of 10 p.p.m. were used for zinc, cadmium, and mercury, and 100 p.p.m. solutions were measured for thallium.

At least two readings of the fluorescence signal for each concentration were made in preparing the working curves. For percentage standard deviation calculations, ten measurements of the fluorescence signals were made for each of the following concentrations: 1, 10, and 100 p.p.m. For thallium these measurements were made on 10, 100, and 1000 p.p.m. solutions rather than on concentrations of 1, 10, and 100 p.p.m. In the case of gases added to the sheath and fuel gases, six readings were taken for each gas added.

Atomic absorption measurements were made using the experimental setup previously described. Readings were made of source intensity with solvent and with sample in the flame and of flame emission background with the source blocked off from the flame and the monochromator-detector. In all cases the amplifier gain was so low that no correction for thermal emission of the sample was necessary. The absorbance for each sample was measured by taking the logarithm of the ratio of the signal due to solvent only in the flame to the signal due to sample in the flame. The thermal emission signal was subtracted from the sample signal prior to the calculation of absorbance.

V. RESULTS AND DISCUSSION

A. Types of Working Curves

From the working curve plot in Figure 5 it is evident that the electrodeless discharge tube was much more effective in producing atomic fluorescence for mercury than was the Hanovia vapor discharge lamp. This was probably due to the greater line intensity of the electrodeless lamp. The mercury electrodeless lamps have been said to be stronger than a d.c. arc, a.c. arc, or condensed spark and to have a Doppler half-width about the same as a water-cooled hollow cathode discharge tube (13). The lines emitted from the electrodeless lamp essentially are not reversed (7). Other excitation sources for mercury were tried, such as the Osram and Philips spectral lamps, but in no case was fluorescence observed.

The working curves for thallium, Figures 9, 16, 17, and 21, involved the use of the thallium electrodeless discharge tube as an excitation source. The thallium Osram spectral lamp was tried, but as in the case of the two mercury lamps of this type, no fluorescence could be obtained. Evidently, the lines produced were either reversed or otherwise of insufficient intensity at the line center. Zinc and cadmium Osram lamps do not fall in the same category, since they were extremely effective in producing atomic fluorescence.

Working curves for zinc (Figures 6, 10, 11, and 18) and cadmium (Figures 7, 12, 13, and 19) were prepared using the respective Osram spectral lamps as excitation sources. The shape of the atomic fluorescence working curves in Figures 6, 7, 10, 11, 12, and 13 agree with the shape predicted by Winefordner and Vickers (39). Regions of low concentration are linear with curvature appearing at high concentrations. Individual curves will be discussed later in greater detail.

Fluorescence was not obtained for the elements gallium, indium, antimony, and selenium when their solutions in the flame were illuminated by electrodeless discharge tube radiation. Measurement of the radiation from these lamps showed that the intensity of the desired lines was considerably below that observed for the sources which were capable of producing fluorescence; in some cases, the difference was of the order of 1000 times lower intensity.

Comparison of the working curves obtained for different fuel gases and atomizer-burners for each of the four fluorescing elements, Figures 6 to 9, shows an interesting trend. For the Beckman total-consumption atomizer-burners the air-hydrogen flame exhibited the highest intensity in all cases. Generally the oxyhydrogen flame was next in the ranking with the oxyacetylene flame having the lowest observed relative fluorescence intensity for these three flames. The Meker burner flame, using natural gas and air, gave results which cannot strictly be compared to those for the total-consumption atomizer-burners because the flame area and path length through this flame were of much greater dimensions than comparable measurements for the Beckman burner flames.

Flame temperatures for the oxyhydrogen and oxyacetylene flames have been calculated for each element by the method of Winefordner, Mansfield, and Vickers (36, 37) according to the position in the flame where fluorescence measurements have been made. Temperature values for the air-hydrogen flame were obtained by comparison of the above values with those listed by Dean (8) and approximating the decrease in temperature. Table 4 lists these temperatures.

Table 4

Flame Temperatures for Various Elements
When Using Beckman Total-Consumption Atomizer-Burners

Flame	Temperature, °K.			
	Zn	Cd	Hg	Tl
H_2/air	1930	1930	1780	1780
H_2/O_2	2620	2620	2480	2480
C_2H_2/O_2	2760	2760	2550	2550

These values seem to indicate a correlation between low flame temperature and maximum relative fluorescence intensity when compared to the working curves for the elements in Figures 6 to 9.

The weak mercury 2537 A. fluorescence when using a Meker burner air-natural gas flame was probably related to the large quenching effects possible when foreign substances are present with mercury vapor, as explained by Pringsheim (22) and Mitchell and Zemansky (19). The nature of this specific flame was different than any of the others because it had a lower temperature (8) and a much higher ratio of flame gases to atomic vapor.

Comparison of the atomic absorption measurements in Figures 18 to 21 with the working curves for atomic fluorescence in Figures 6 to 9 will give an idea of the efficiency of excitation of fluorescence for each element. Zinc, cadmium, and mercury showed high absorbance which would account for the favorable results obtained by atomic fluorescence measurements. Thallium, however, showed very poor absorption when compared to the other elements. This would partially explain the fact that thallium did not fluoresce as well as the other elements. The low values for the air-natural gas fluorescence working curve for mercury can be explained by comparing it with the working curve for atomic absorption under the same conditions. Here also the air-natural gas flame gave poorer results than the other flames. If an atomic vapor in a flame does not absorb radiation well, then the fluorescence should also be low.

Different solvents used for analysis by atomic fluorescence flame spectrometry should affect the relative fluorescence intensity as measured according to the efficiency of solvent evaporation in the flame and their flow rates into the flame. This is a result of the viscosities of the solutions (35). Solutions in water, 30% methanol in water, and 70% methanol in water were used to obtain the working curves shown in Figures 10 to 17. For both the oxyhydrogen and the oxyacetylene flames in the cases of zinc, cadmium, and thallium, the order of decreasing intensity by solvents was 70% methanol, 30% methanol, and water. Because the solutions with the higher percentages of methanol should be the ones which would evaporate easiest, this seems to be the dominant factor in influencing the position of these curves. In the curves for mercury in Figures 14 and 15 there seems to be a different trend indicated with the 30% methanol solutions having the lowest relative fluorescence intensities and the other two solvents having higher intensities. In most cases the water solution of mercury had a higher intensity signal than the 70% methanol signal.

Data obtained on the viscosities of methanol-water mixtures indicated that a maximum of viscosity for the system existed near the composition of 30% methanol. At the height above the flame used for the analysis of mercury, the solvent droplets would be more completely evaporated than lower in the flame, so the effect on intensity produced by solvent viscosity would overshadow that of solvent evaporation, which was more important for the other elements.

B. Types of Gases Added to Fuel Gas

Addition of foreign gases to the flame should have three main effects: the temperature of the flame should be lowered, the fluorescence should be quenched by collisional deactivation of excited atoms, and the flame gases should be diluted. The two flames on which the effect of addition of argon and nitrogen to the flame by mixing with the fuel gas was studied exhibited opposite trends in the change observed in relative fluorescence intensity. In the oxyhydrogen flame, the addition of either gas gave readings lower than those obtained when no gas was added. Argon and nitrogen probably acted as quenching species in the flame with nitrogen having a greater effect due to its molecular form (1). The data for the two flames can be found in Tables 8 to 11.

Using the oxyacetylene flame, the trend was reversed; argon and nitrogen addition resulted in a higher intensity than the normal flame. In this case the observed increase could possibly have been due to a decrease in the temperature of the flame or a dilution of the flame gases, which could be seen as quenching species. The oxyacetylene flame will have a higher CO_2 content than the oxyhydrogen flame. Alkemade (1) found CO_2 to be extremely effective in quenching flame fluorescence of sodium. A dilution of the flame gases would reduce the probability of collisions between activated atoms and CO_2 molecules. Slightly higher readings were obtained for argon than for nitrogen in the oxyacetylene flame. This could be explained by reasoning that molecular nitrogen was much more efficient in quenching fluorescence by collisional deactivation of the excited atoms than was atomic argon (1). For thallium in the oxyacetylene flame the results obtained showed that nitrogen addition gavc the lowest intensities, which was probably due to the quenching effects of nitrogen on thallium vapor.

C. Types of Gases Added to Burner Sheath

Use of a sheathed oxyhydrogen flame gave no definite indications of its value for use in atomic fluorescence flame spectrometry. For zinc analyses, argon in the sheath generally gave higher intensity values as well as having higher signal-to-noise ratios for aqueous solutions as seen in Table 8. The percentage standard deviation, however, was higher for the use of the sheath for all gases than when the sheath was not used. In the case of mercury, as seen in Table 10, no definite increase in fluorescence intensity due to the sheath gases could be seen, but the percentage standard deviation was lower for aqueous and 30% methanol solutions. All gases had about the same effect. Argon seemed to give a better signal-to-noise ratio when it was used in the sheath. The sheathed flame was found to be unstable to the extent that it would frequently be self-extinguished. The use of the sheathed flames, therefore, is not sufficiently justified.

D. Comparison of Types of Flame Spectrometry

Atomic fluorescence flame spectrometry compared favorably with atomic absorption and atomic emission flame spectrometry as seen in Tables 5, 6, and 7. The limit of detection in atomic fluorescence has been defined as "that concentration of fluorescent species which produces a photodetector signal due to fluorescence approximately 0.75 times as large as the root-mean-square noise signal" (38).

Table 5

Limit of Detection in p.p.m. for Various Elements for Atomic Fluorescence Flame Spectrometry

Flame	Solvent	Element			
		Zn	Cd	Hg	Tl
H_2/O_2	H_2O	0.04	0.1	0.1	1.0
	30% CH_3OH	0.03	0.1	0.1	1.0
	70% CH_3OH	0.005	0.1	0.1	---
C_2H_2/O_2	H_2O	0.04	0.3	0.1	5.0
	30% CH_3OH	0.005	0.3	0.1	5.0
	70% CH_3OH	0.01	0.2	0.3	---
H_2/air	H_2O	0.02	0.2	0.1	2.0
Natural gas /air	H_2O	0.01	0.1	7.0	1.0

A simple comparison of these three tables will show that atomic fluorescence flame spectrometry is the most sensitive technique of the three available for analysis of zinc and mercury, and it only falls slightly short of being the best method for cadmium. Lower limits of detection were possible for zinc and cadmium (15), but these have been obtained by special atomic absorption techniques using a 91 cm. cell. Atomic absorption and atomic emission gave considerably lower limits of detection for the analysis of thallium.

Table 6

Limit of Detection in p.p.m. for Various Elements for Atomic Emission Flame Spectrometry (17)

Element	Wavelength, A.	Flame	Solvent	Limit
Zn	2139	H_2/O_2	H_2O	500
			organic	10
		C_2H_2/O_2	H_2O	600
		H_2/air	H_2O	2500
	5200	C_2H_2/O_2	organic	2.5
Cd	2288	H_2/O_2	H_2O	10
		C_2H_2/O_2	H_2O	40
		H_2/air	H_2O	50
	3261	H_2/air	H_2O	0.5
Hg	2537	H_2/O_2	H_2O	30
			organic	6
		C_2H_2/O_2	H_2O	50
		H_2/air	H_2O	10
Tl	3776	H_2/O_2	H_2O	0.1
			organic	0.06
		C_2H_2/O_2	H_2O	1
		H_2/air	H_2O	0.2

Table 7

Limit of Detection in p.p.m. for Various Elements for Atomic Absorption Flame Spectrometry (16, 25)

Flame	Solvent	Element			
		Zn	Cd	Hg	Tl
H_2/O_2	H_2O	0.3	1	100	0.2
	organic	0.08	0.1	100	---
Natural gas /air	H_2O	0.03	0.03	10	---

Since atomic absorption flame spectrometry offers the closest competition for atomic fluorescence, the fact should be mentioned that the absorption measurements listed were made using a flame cell 10 to 12 cm. long and radiation line sources whose cost exceeds that of those used for fluorescence. Thus, atomic fluorescence is a more convenient and inexpensive method of analysis than is atomic absorption for the cases described.

In order to compare the results obtained for the atomic fluorescence of thallium in flames with atomic emission flame spectrometry, measurements were made according to standard techniques of atomic emission flame spectrometry. The experimental setup used for atomic emission measurements was exactly the same as used for the fluorescence studies; however, in this case the thermally emitted radiation from the outer cone of the flame was observed (the thallium discharge tube was turned off in this case). Figure 22 shows the working curves obtained and indicates that atomic emission was as good or better than atomic fluorescence for the analysis of thallium. Since fluorescence measurements were made using the outer cone of the natural gas-air flame, emission readings were not taken for this flame.

E. Accuracy and Signal-to-Noise Ratio

The percentage standard deviation for a number of measurements at a given concentration was calculated (18) by

$$\%\sigma = \frac{100}{\bar{I}_F} \left[\frac{\sum (I_F - \bar{I}_F)^2}{n - 1} \right]^{1/2} , \qquad (\underline{2})$$

where $\%\sigma$ is the percentage standard deviation and $\bar{I}_F$ is the mean average of n readings of the relative fluorescence intensity, I_F. The signal-to-noise ratio was calculated from the root-mean-square noise value according to

$$S/N = \bar{I}_F/N \quad , \qquad (\underline{3})$$

where S/N is the signal-to-noise ratio and N is the root-mean-square noise figure (0.354 of peak-to-peak noise).

The values obtained for percentage standard deviation are listed in Tables 8 to 11 for the elements which were considered. The percentage standard deviations can be compared with average values of 2% for atomic absorption (12) and 0.2% to 5% for atomic emission (18). For zinc the percentage of standard deviations were mostly below 5% for all concentrations while for cadmium and mercury this range was valid only above concentrations of 10 p.p.m.

A reproducibility of 11% to 27% was obtained for 1 p.p.m. solutions of cadmium and mercury. Thallium exhibits the same variation as cadmium and mercury but at concentrations higher by a factor of ten.

The signal-to-noise readings varied in the opposite manner of the results obtained for the percentage standard deviations. Higher values for the signal-to-noise ratio are desirable because this indicates either a high intensity signal, a low noise level, or a combination of these two factors. Higher values are also an indication of the ease with which readings of fluorescence intensity have been made at those concentrations. High signal-to-noise ratios were found for all concentrations of zinc and higher concentrations of cadmium, mercury, and thallium. High noise levels and low signal levels were present for low concentrations of cadmium, mercury, and thallium.

VI. FUTURE APPLICATIONS OF ATOMIC FLUORESCENCE FLAME SPECTROMETRY TO CHEMICAL ANALYSIS

A. Shapes of Working Curves

The theoretical shape of a working curve plot of intensity of fluorescence vs. ground state atom concentration has been predicted by Winefordner and Vickers (39). At low concentrations the plot is essentially linear; as the concentration increases the curve reaches a maximum and then decreases in value. This is the shape which has been observed in actual practice, as seen in Figures 6 and 7, the working curves for zinc and cadmium. Mercury and thallium (Figures 8 and 9) did not exhibit this curvature because their high atomic weights placed these concentrations in molarity at lower values than zinc and cadmium.

The region of the working curves most suitable for use in practical analysis is that in which linearity exists. In the curved region of the maximum, an error in the intensity measurement would be magnified on the concentration scale, and so upper limits of analysis must be set for these elements. The approximate upper limits for zinc, cadmium, mercury, and thallium are 10 p.p.m., 100 p.p.m., 1000 p.p.m., and 1000 p.p.m. respectively for total-consumption atomizer-burners. Higher limits are probable in the cases of mercury and thallium (1000 p.p.m. was the upper limit of the study). Using the Meker burner the upper limit is 1000 p.p.m. in all cases.

In order to use flame fluorescence as a routine analytical method one should first plot an accurate working curve, using a series of standard solutions of different concentrations, under the conditions to be used for analysis, in order to determine the behavior of the working curve for the element with respect to curvature at different concentrations. Once this curve has been plotted one needs only to run solutions varying by powers of ten in order to prepare a working curve suitable for a series of analyses.

B. Improvement of Equipment

Sources. Probably the one most important item in the atomic fluorescence instrument is the source which produces the excitation. As Winefordner and Vickers (39) have shown for low sample concentrations,

$$I_F = CP^{\circ}N_{\circ}, \qquad (4)$$

where I_F is the measured fluorescence intensity, C is a constant for a particular system, P° is the incident radiant power from the source, and $N_{\circ}$ is the ground state atom concentration. Thus, a variation of 1% in the source will be seen directly as a variation of 1% in the fluorescence intensity. The most stable source will give the best accuracy if all other factors are constant.

Also from the equation above one can easily see that the greater the intensity of the source, the greater will be the intensity of the fluorescence. One should attempt, therefore, to use a source of as high stability and intensity as possible.

A source can be intense, but if it exhibits a significant amount of line reversal, the very portion of the radiation needed for excitation is lost. Therefore, absence of reversal of the line source should also be of primary importance.

Several sources show promise of being valuable for use in atomic fluorescence flame spectrometry. A water-cooled mercury arc which emits unreversed lines should be extremely suited to use in mercury analysis. The above arc could be extended to other metals through the use of amalgams, such as a thallium amalgam arc as used by Nichols and Howes for excitation of thallium fluorescence (20). Inclusion of trace quantities of elements in the carbon rods of a d.c. arc (2) could be used in many cases as a means of exciting fluorescence, especially if no other source is available. Finally, an extremely high intensity source emitting a continuum, e.g., a 1000 watt xenon arc lamp, would be suitable for excitation of fluorescence of all elements if the source intensity is high enough at the exact value of the required line. A 100 watt xenon arc has been tried as a source, but its intensity was not sufficiently high.

Atomizer-Burners. Because the burner is essentially a sample cell, under ideal conditions it would be a large vessel holding only the atomic vapor of the element under investigation. Herrmann and Alkemade (18) feel that the most efficient atomizer-burner for atomic emission flame spectrometry is the total-consumption direct-injection burner such as that manufactured by Beckman Instruments. In flame fluorescence, however, light scattering by unevaporated solvent droplets is important, and the Beckman burner does produce a more coarse spray and therefore more scattering of source radiation than a chamber-atomizer coupled to a burner. A chamber-atomizer, therefore, would be more efficient in reducing the scattering of the source radiation. Actually, the Beckman burner should be a better choice because it might give a larger concentration of atoms in the flame due to a higher solution flow rate. This would depend upon the specific chamber-atomizer chosen and its efficiency in introducing the solution vapor into the flame as compared with the efficiency of the Beckman burner. The use of nonaqueous solvents results in a considerable increase in sample introduction efficiency (36) when using total-consumption atomizer-burners. Therefore, it is doubtful whether chamber-type atomizer-burners would even have a resultant advantage over total-consumption atomizer-burners.

The size of the flame with respect to its diameter should also be considered. According to Winefordner and

Vickers (39) the fluorescence intensity should increase with the path length through the flame taken by the source radiation. A wider flame than produced by the Beckman total-consumption atomizer-burner should give better results. In the case of a wide flame, however, a lens would be needed in front of the entrance slit of the monochromator so that all of the flame would be "seen" by the monochromator.

Each element being analyzed probably has an optimum flame temperature, so differences in the gases used would also affect the design of a burner. The gases chosen should not have reaction products which will quench the fluorescence as Alkemade (1) found was true of CO_2 with respect to sodium fluorescence in a flame.

Monochromators and Detectors. Because most of the excitation sources used for atomic fluorescence flame spectrometry produce broad lines, solvent droplet scattering will reflect a fraction of this radiation into the monochromator. In some cases the flame itself has an intense background. Ideally, the monochromator should be capable of resolving only the fluorescence line itself and eliminating the effects of scattering as well as most of the flame noise. One would expect the best results, therefore, from a spectrometer of high resolving power.

Most fluorescence measurements will probably be made in the ultraviolet region of the spectrum. It is essential, therefore, that all optics be made of quartz to eliminate attenuation of the fluorescence or source radiation by optical absorption. The photomultiplier detector tube, usually a 1P28, should have a quartz outer envelope. In the visible region better signal-to-noise ratios would be possible by using a 1P21 photomultiplier tube which has a glass envelope (24).

Amplifier. Consideration must also be given to the amplifiers, which convert the signal from the photomultiplier tube detector into a form which can be read or recorded. In the ultraviolet region of the spectrum the thermal emission is low, and so a d.c. amplifier can be used. Sensitivity and stability are the two primary factors affecting the selection of an amplifier. The amplifier must be sensitive enough to detect the slightest variations above the dark current output of the photomultiplier detector. Stability is necessary so that the measurements made will be constant and reproducible.

When measurements are made in the visible region, the flame background is high and thermal emission is more probable. If the fluorescence is modulated at a constant frequency by means of a chopper placed between the source and the flame, then a tuned a.c. amplifier can be used to amplify only the fluorescence. The thermal emission is primarily a d.c. signal, and so no correction for its presence need be made. A further refinement of this technique would be to use a tuned a.c. amplifier, which would amplify only signals of the chopper frequency and attenuate all others. Because the fluctuation of the flame background results in a white noise, the flame background interference could be reduced even further by a narrow band amplifier.

C. Sensitized Fluorescence

A specialized technique of atomic fluorescence flame spectrometry is sensitized fluorescence. This technique may be of special value in cases where excitation sources are not available. An example of this would be the introduction of a mixture of thallium and mercury in solution form into a flame illuminated by a source of mercury resonance radiation. The thallium atoms would be excited by energy transfer collisions with mercury atoms activated by absorption of resonance radiation. This technique was tried, but no thallium radiation could be detected.

D. The Value of Atomic Fluorescence Flame Spectrometry as a Means of Chemical Analysis

Atomic fluorescence flame spectrometry definitely has use as a method of analysis. It should complement the existing methods of atomic emission and atomic absorption flame spectrometry. Elements whose resonance lines lie in the ultraviolet and which give poor results by atomic emission should be adaptable to analysis by atomic fluorescence as well as atomic absorption, which was the only alternate spectrometric method. Also, elements which absorb weakly in this region, e.g., mercury at 2537 A., may be well suited to analysis by atomic fluorescence if their quantum efficiencies are favorable. The other important advantage atomic fluorescence has over atomic absorption is that fluorescence excitation sources are generally less expensive than hollow cathode discharge tubes. The value of atomic fluorescence flame spectrometry for routine analyses should give it a place in the large number of methods available to the analyst.

VII. SUMMARY

Atomic fluorescence flame spectrometry was applied to the analysis of solutions of zinc, cadmium, mercury, and thallium. Solutions of these elements were introduced into a flame and the resulting atomic vapor was excited by radiation from an intense, unreversed line source. The resulting fluorescence emission was measured at right angles to the source-flame axis by means of a compact monochromator-detector and a sensitive d.c. amplifier. The wavelengths used for analysis were 2139 A., 2288 A., 2537 A., and 3776 A. for zinc, cadmium, mercury, and thallium, respectively.

Different excitation sources were tried and compared. Working curves were prepared using air-hydrogen, oxyhydrogen, and oxyacetylene flames with total-consumption atomizer-burners and an air-natural gas flame with a Meker burner and chamber atomizer. These curves were linear over a large range of concentrations with curvature appearing only at high values of concentration. The influence of 30% methanol and 70% methanol solvents as well as water on the shapes of working curves and limits of detection for each element was studied in detail. Argon and nitrogen were premixed with the fuel gas and argon, nitrogen, and oxygen were added to a burner sheath to observe possible effects on the fluorescence. Atomic absorption measurements were made for purposes of rough quantum efficiency comparisons. Percentage standard deviations and signal-to-noise ratios were determined for all studies.

The limits of detection obtained for zinc, cadmium, mercury, and thallium were, respectively, 0.01, 0.1, 0.1, and 1.0 p.p.m. for aqueous solutions. Low flame temperatures and maximum intensity seemed to be related. The 70% methanol solutions resulted in the maximum sensitivity except in the case of mercury where water was the best solvent. Gases added to the oxyhydrogen flame lowered the fluorescence intensity while for the oxyacetylene flame an increase was noted. Argon had the greatest effect. No justification was found for using the burner sheath for the elements studied in this work. Atomic fluorescence flame spectrometry was found to compare favorably with atomic absorption flame spectrometry for analysis of zinc, cadmium, and mercury. However, the percentage standard deviation of 5% was somewhat higher than representative values for atomic absorption methods.

The history and theory of atomic fluorescence flame spectrometry were described in brief. Suggestions were made for improvement of the method by selection of proper components for the experimental setup. After more extensive research, development, and application, atomic fluorescence flame spectrometry should become an accepted laboratory method of analysis for a number of elements.

APPENDIX A

WORKING CURVES

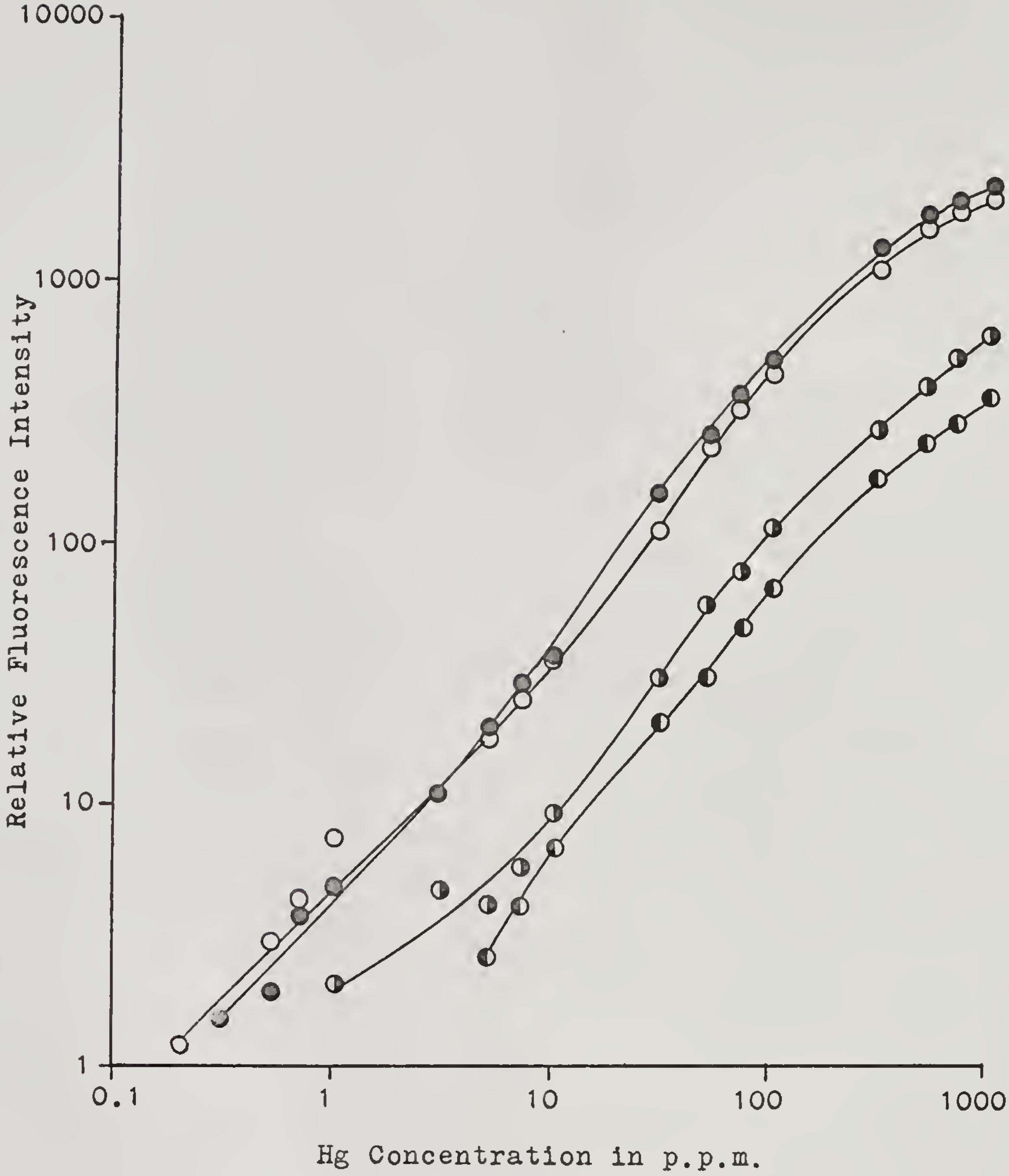

Figure 5. Atomic Fluorescence Working Curves for Mercury (Hg 2537 A. Line) in Oxyhydrogen and Oxyacetylene Flames Using a Vapor Discharge Tube and an Electrodeless Discharge Tube

○ H_2/O_2, Electrodeless Discharge Tube

● C_2H_2/O_2, Electrodeless Discharge Tube

◐ H_2/O_2, Vapor Discharge Tube

◑ C_2H_2/O_2, Vapor Discharge Tube

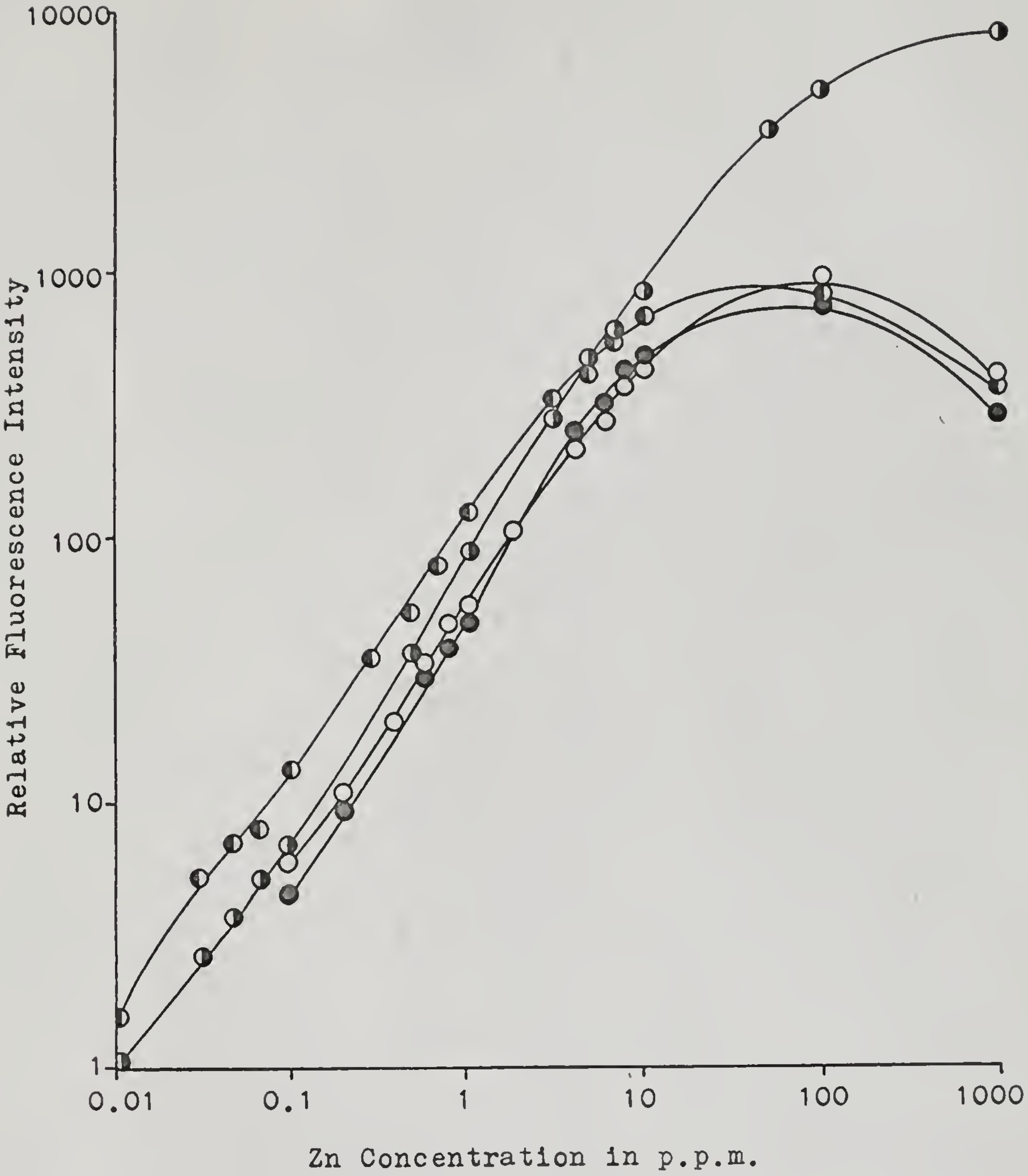

Figure 6. Atomic Fluorescence Working Curves for Zinc (Zn 2139 A. Line) Introduced as Aqueous Solutions into Different Flames

○ H_2/O_2
● C_2H_2/O_2
◐ H_2/air
◑ Natural gas/air

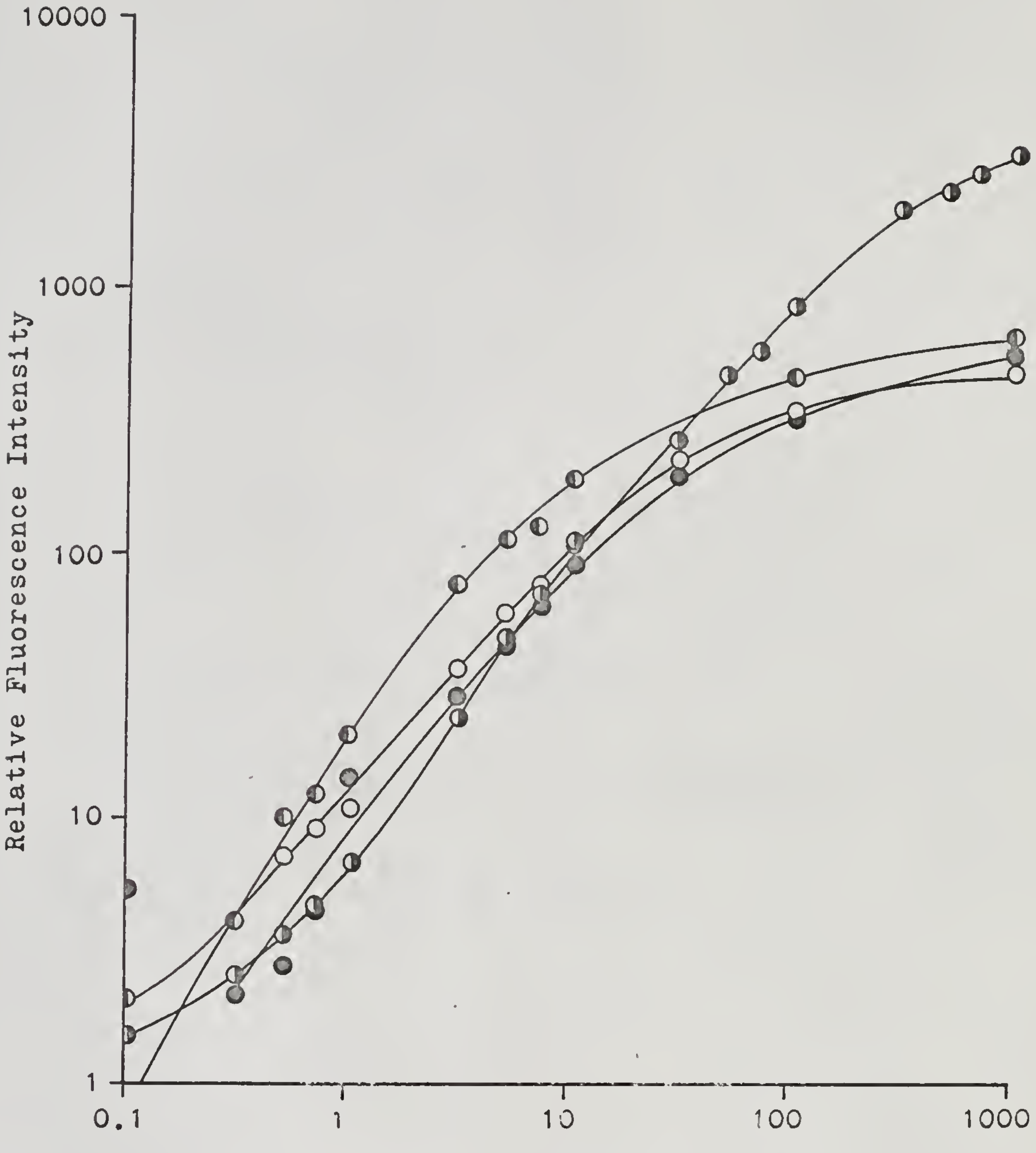

Figure 7. Atomic Fluorescence Working Curves for Cadmium (Cd 2288 A. Line) Introduced as Aqueous Solutions into Different Flames

○ H_2/O_2

● C_2H_2/O_2

◐ H_2/air

◑ Natural gas/air

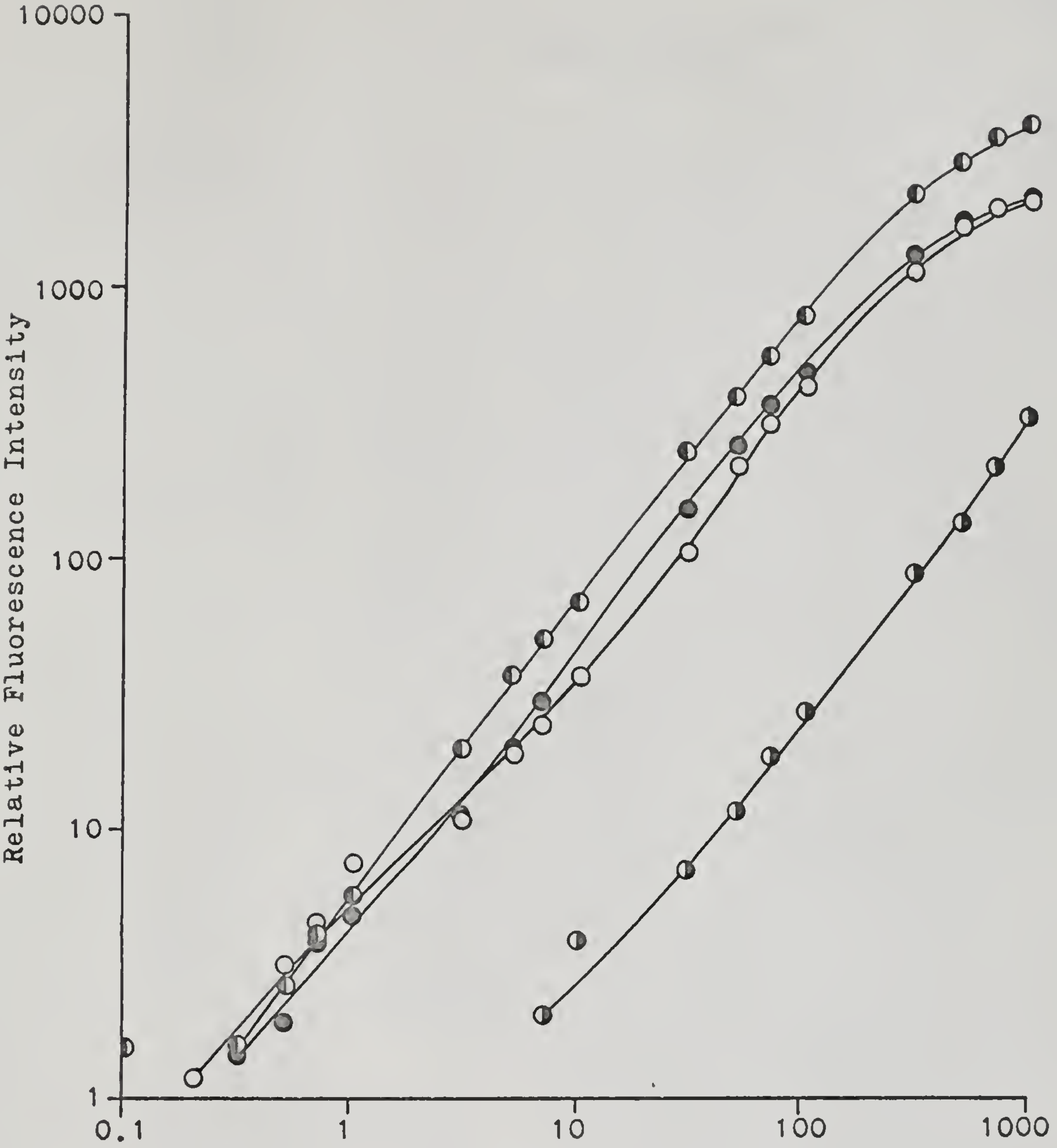

Figure 8. Atomic Fluorescence Working Curves for Mercury (Hg 2537 A. Line) Introduced as Aqueous Solutions into Different Flames Excited by the Electrodeless Discharge Tube

○ H_2/O_2

● C_2H_2/O_2

◐ H_2/air

◑ Natural gas/air

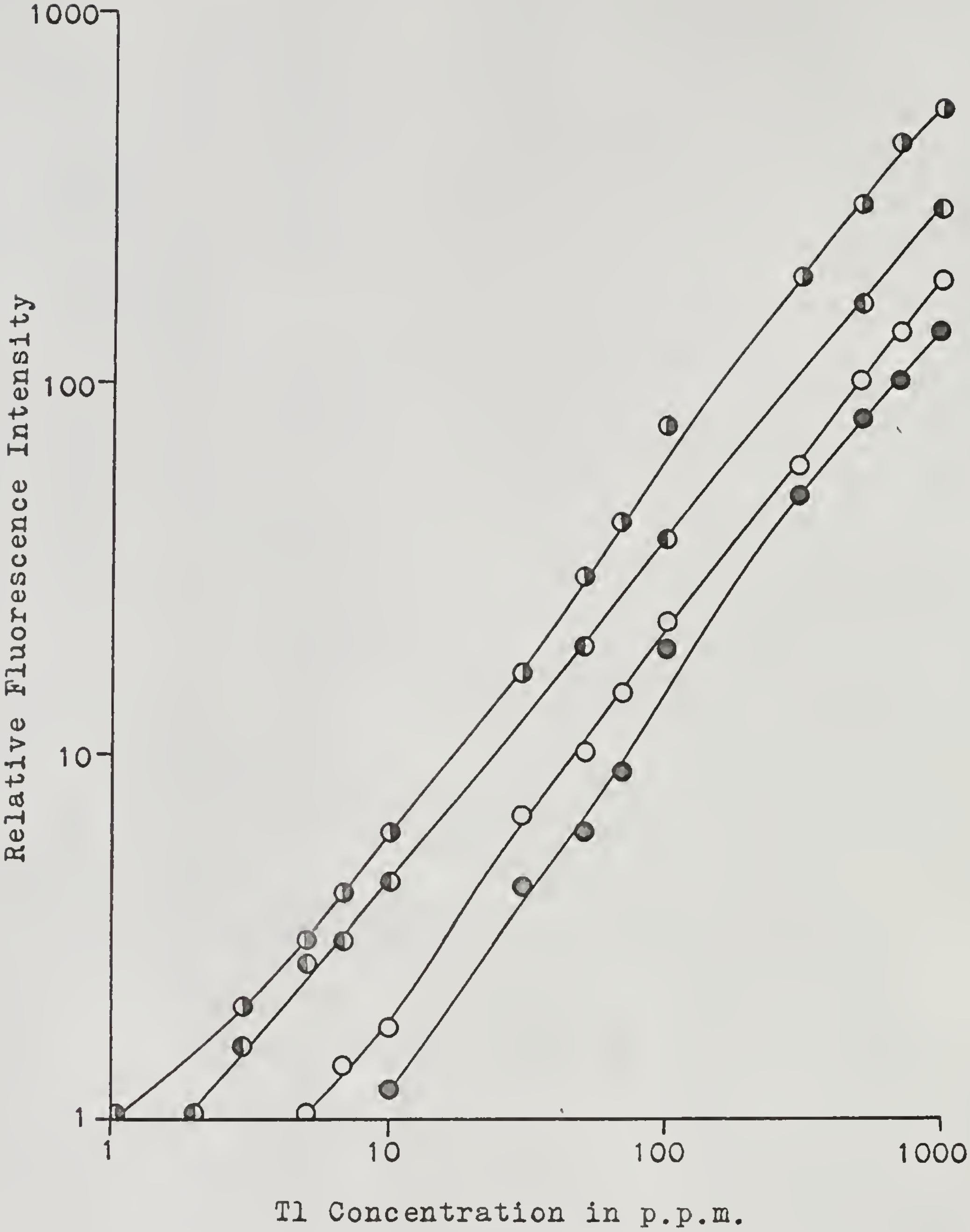

Figure 9. Atomic Fluorescence Working Curves for Thallium (Tl 3776 A. Line) Introduced as Aqueous Solutions into Different Flames

○ H_2/O_2
● C_2H_2/O_2
◐ H_2/air
◑ Natural gas/air

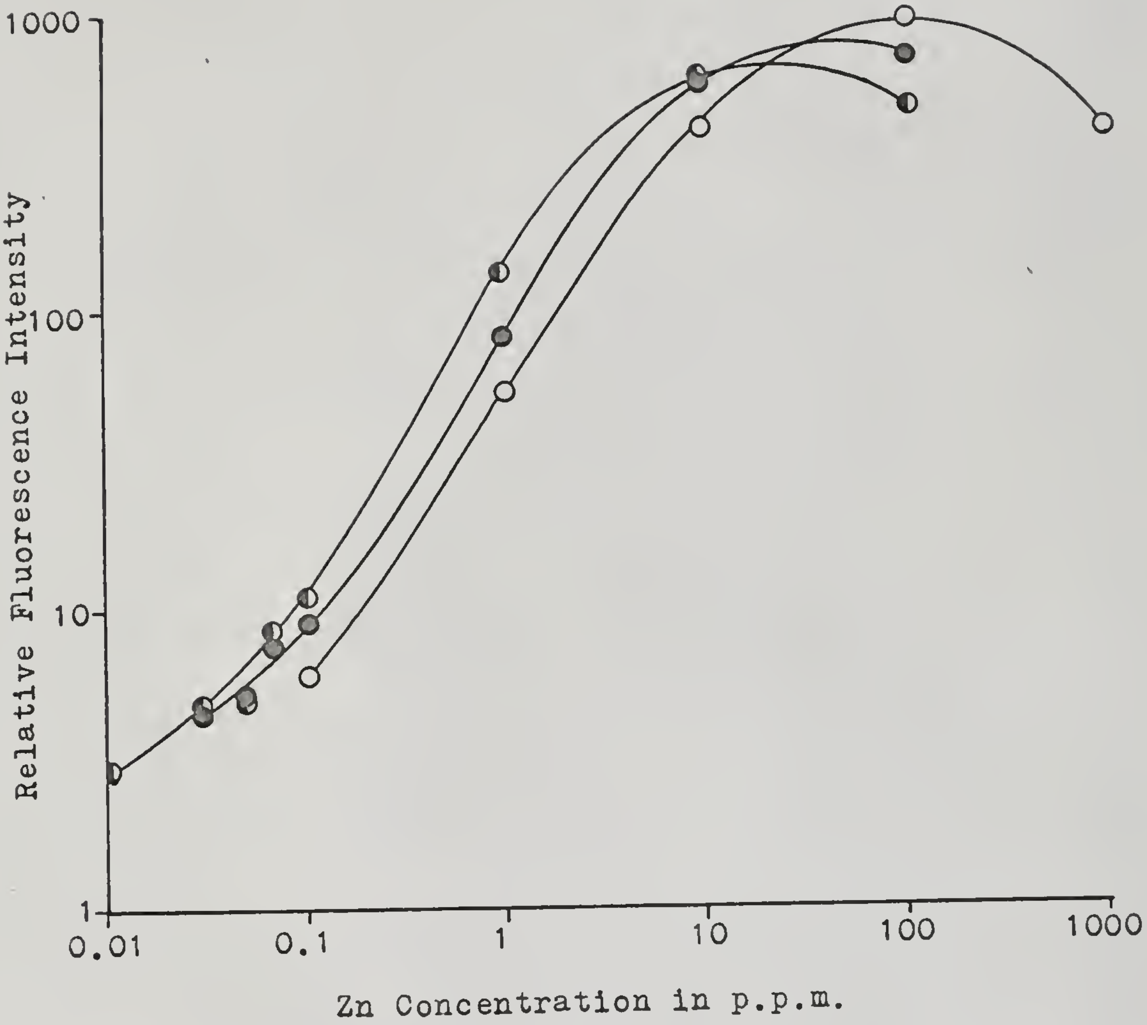

Figure 10. Atomic Fluorescence Working Curves for Zinc (Zn 2139 A. Line) in Different Solvents Introduced into the Oxyhydrogen Flame

○ H_2O

● 30% CH_3OH

◐ 70% CH_3OH

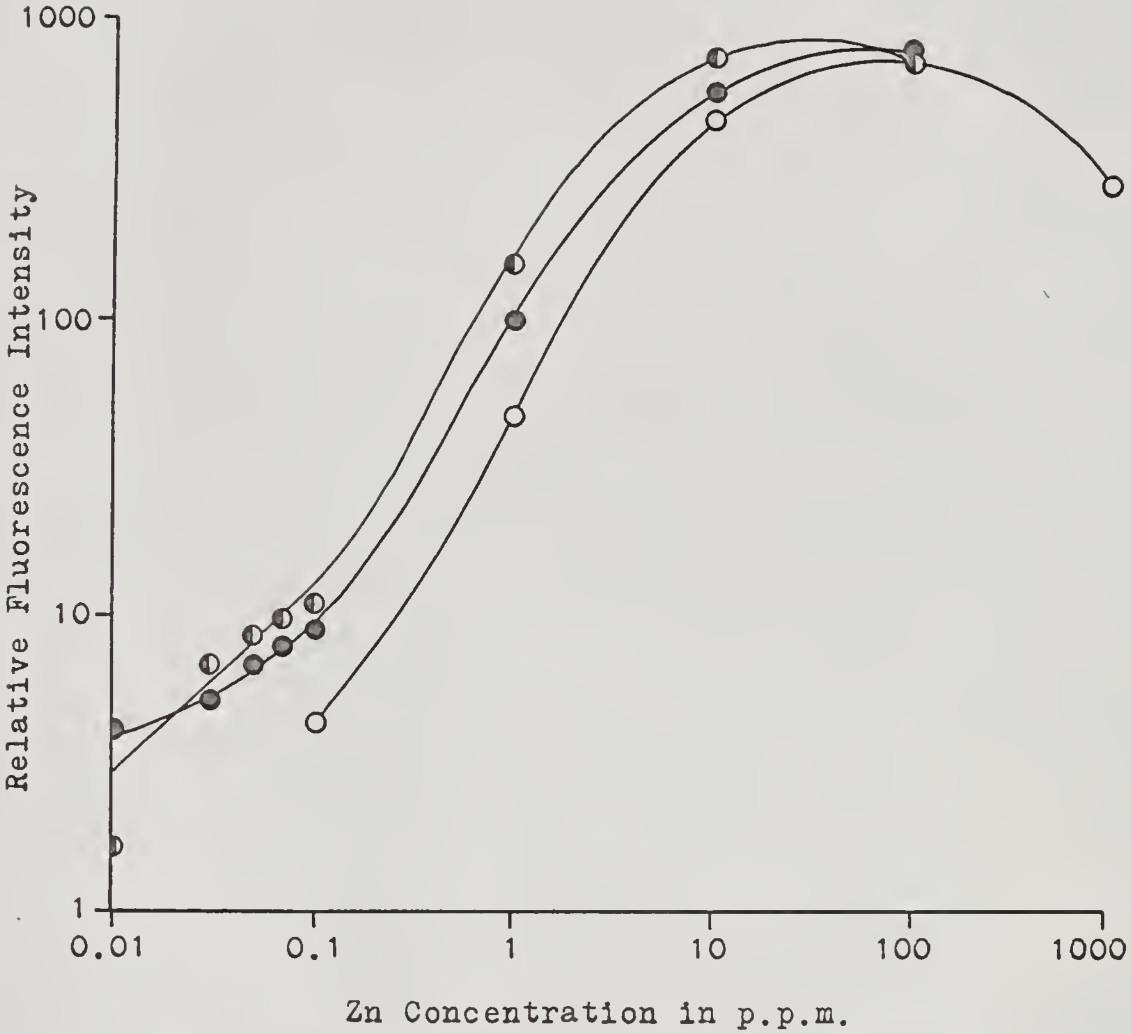

Figure 11. Atomic Fluorescence Working Curves for Zinc (Zn 2139 A. Line) in Different Solvents Introduced into the Oxyacetylene Flame

○ H_2O
● 30% CH_3OH
◐ 70% CH_3OH

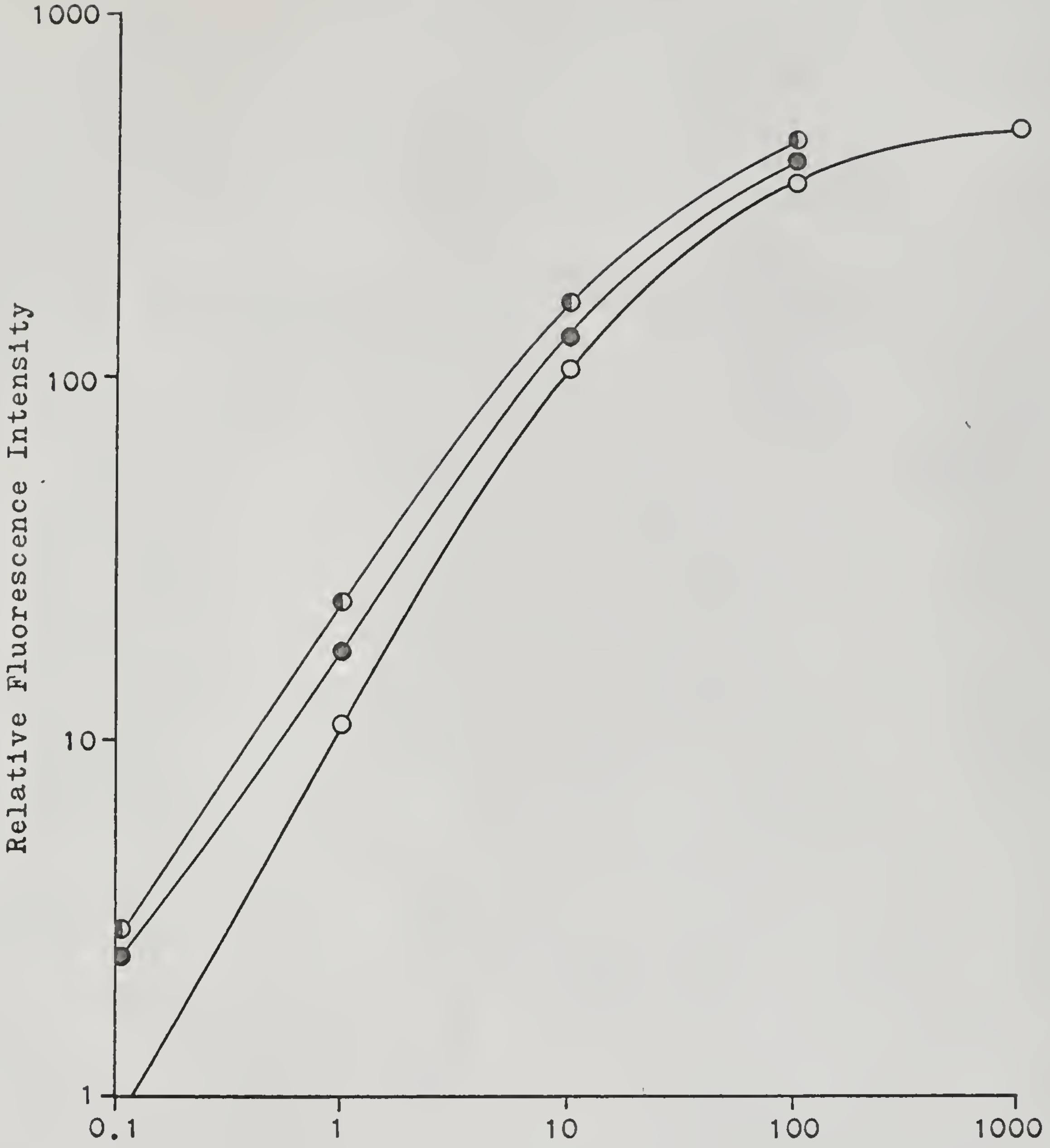

Figure 12. Atomic Fluorescence Working Curves for Cadmium (Cd 2288 A. Line) in Different Solvents Introduced into the Oxyhydrogen Flame

○ H_2O

● 30% CH_3OH

◐ 70% CH_3OH

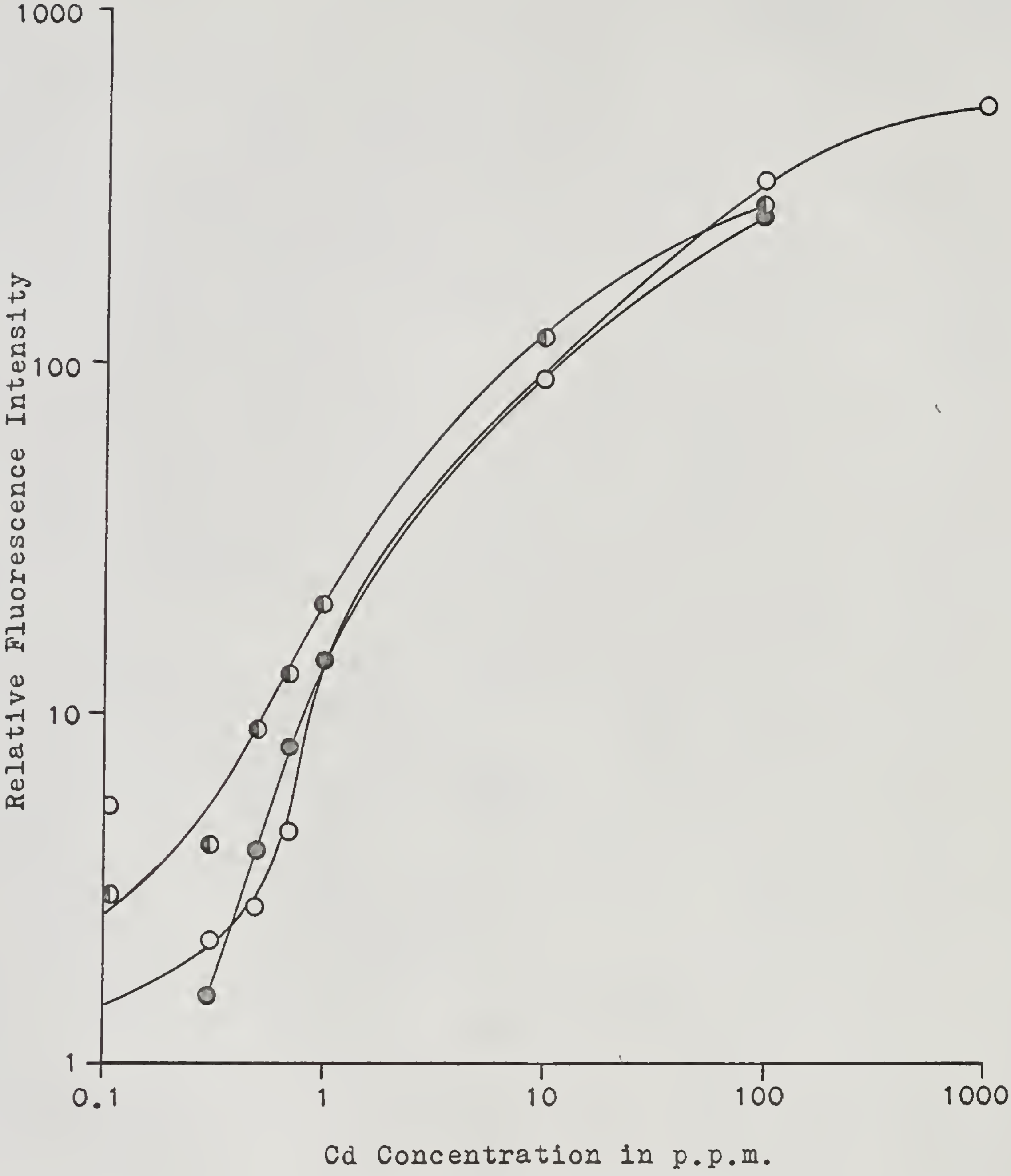

Figure 13. Atomic Fluorescence Working Curves for Cadmium (Cd 2288 A. Line) in Different Solvents Introduced into the Oxyacetylene Flame

○ H_2O

● 30% CH_3OH

◐ 70% CH_3OH

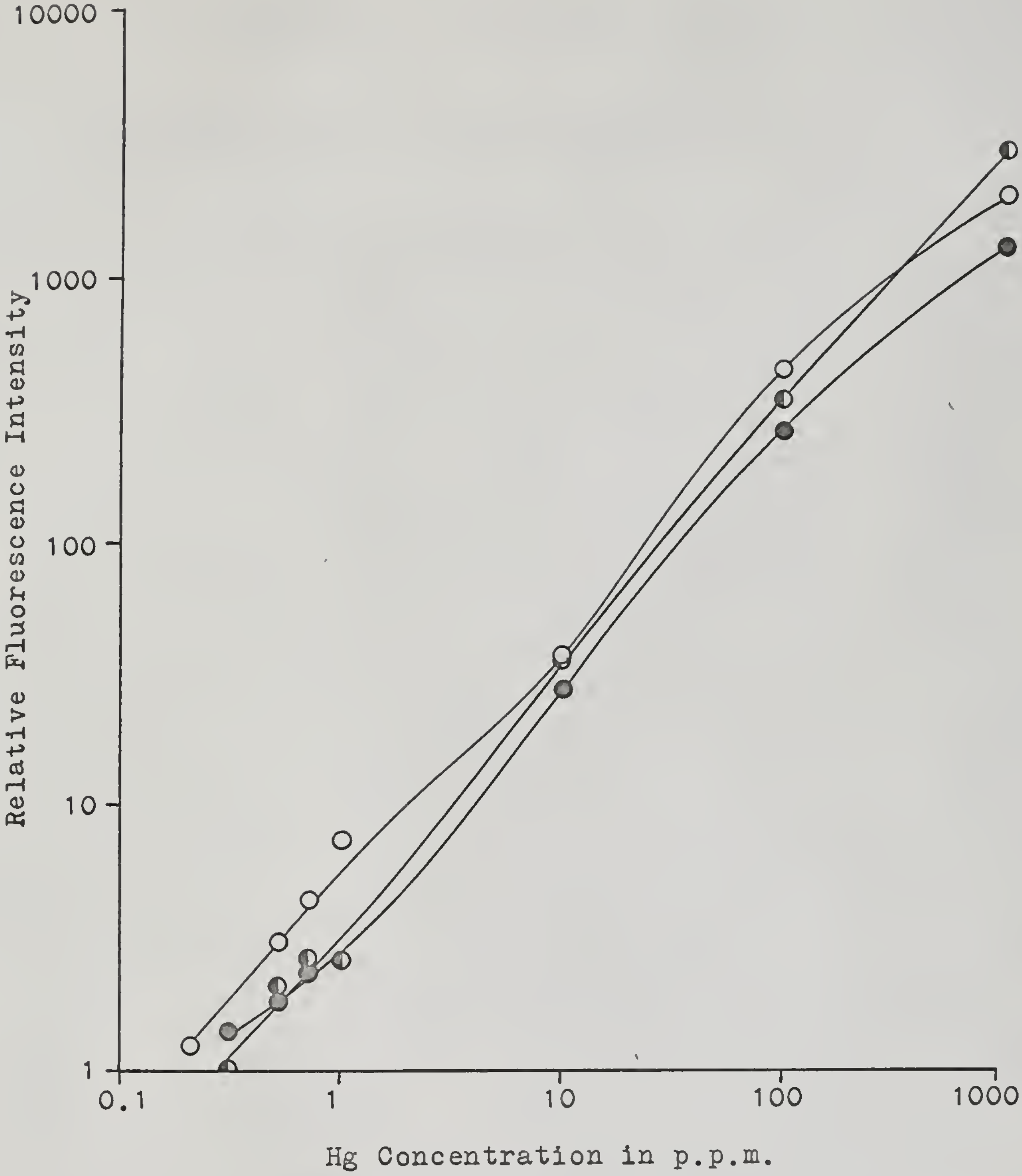

Figure 14. Atomic Fluorescence Working Curves for Mercury (Hg 2537 A. Line) in Different Solvents Introduced into the Oxyhydrogen Flame Excited by the Electrodeless Discharge Tube

○ H_2O

● 30% CH_3OH

◐ 70% CH_3OH

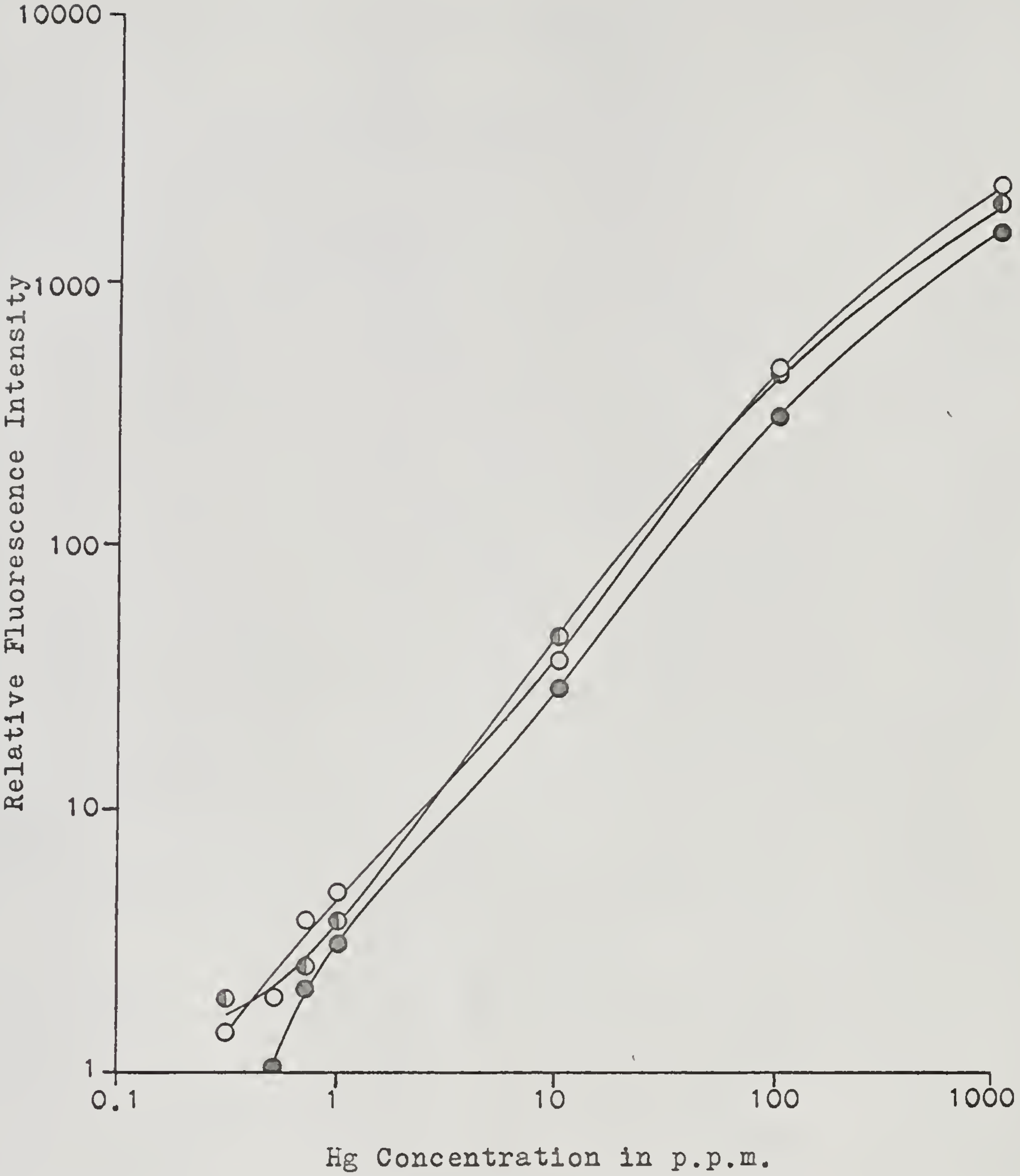

Figure 15. Atomic Fluorescence Working Curves for Mercury (Hg 2537 A. Line) in Different Solvents Introduced into the Oxyacetylene Flame Excited by the Electrodeless Discharge Tube

○ H_2O

● 30% CH_3OH

◐ 70% CH_3OH

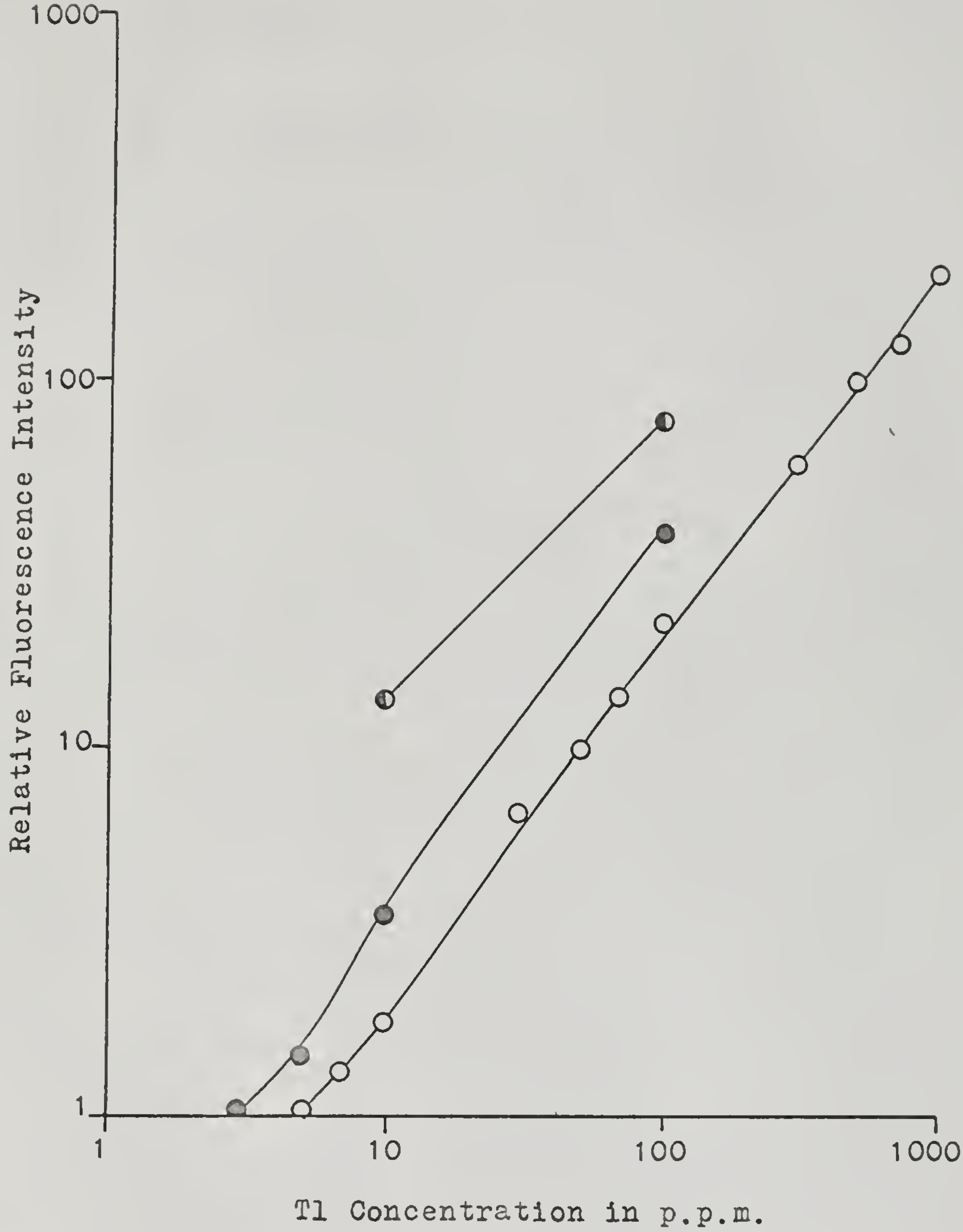

Figure 16. Atomic Fluorescence Working Curves for Thallium (Tl 3776 A. Line) in Different Solvents Introduced into the Oxyhydrogen Flame

○ H_2O

● 30% CH_3OH

◐ 70% CH_3OH

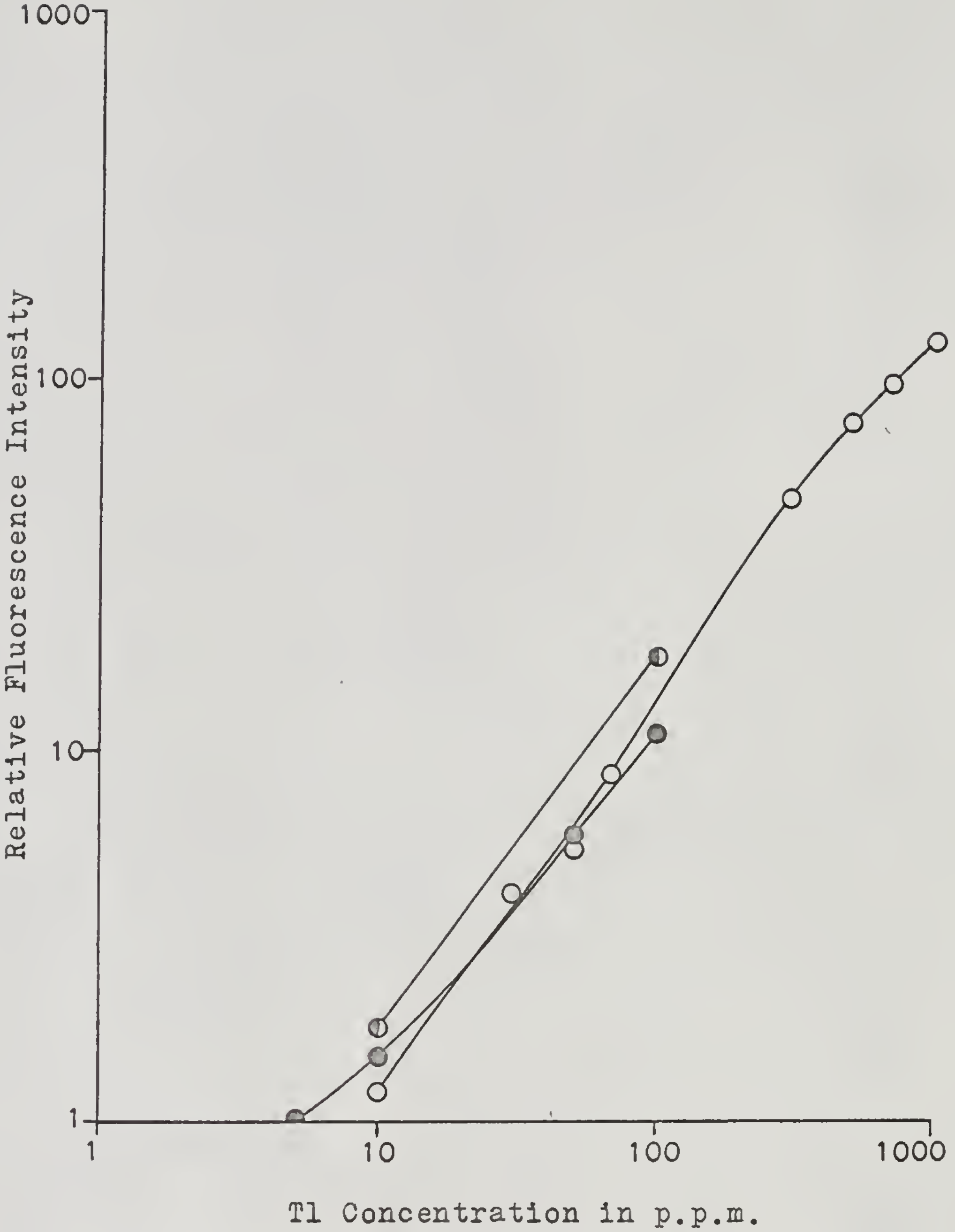

Figure 17. Atomic Fluorescence Working Curves for Thallium (Tl 3776 A. Line) in Different Solvents Introduced into the Oxyacetylene Flame

○	H_2O
●	30% CH_3OH
◐	70% CH_3OH

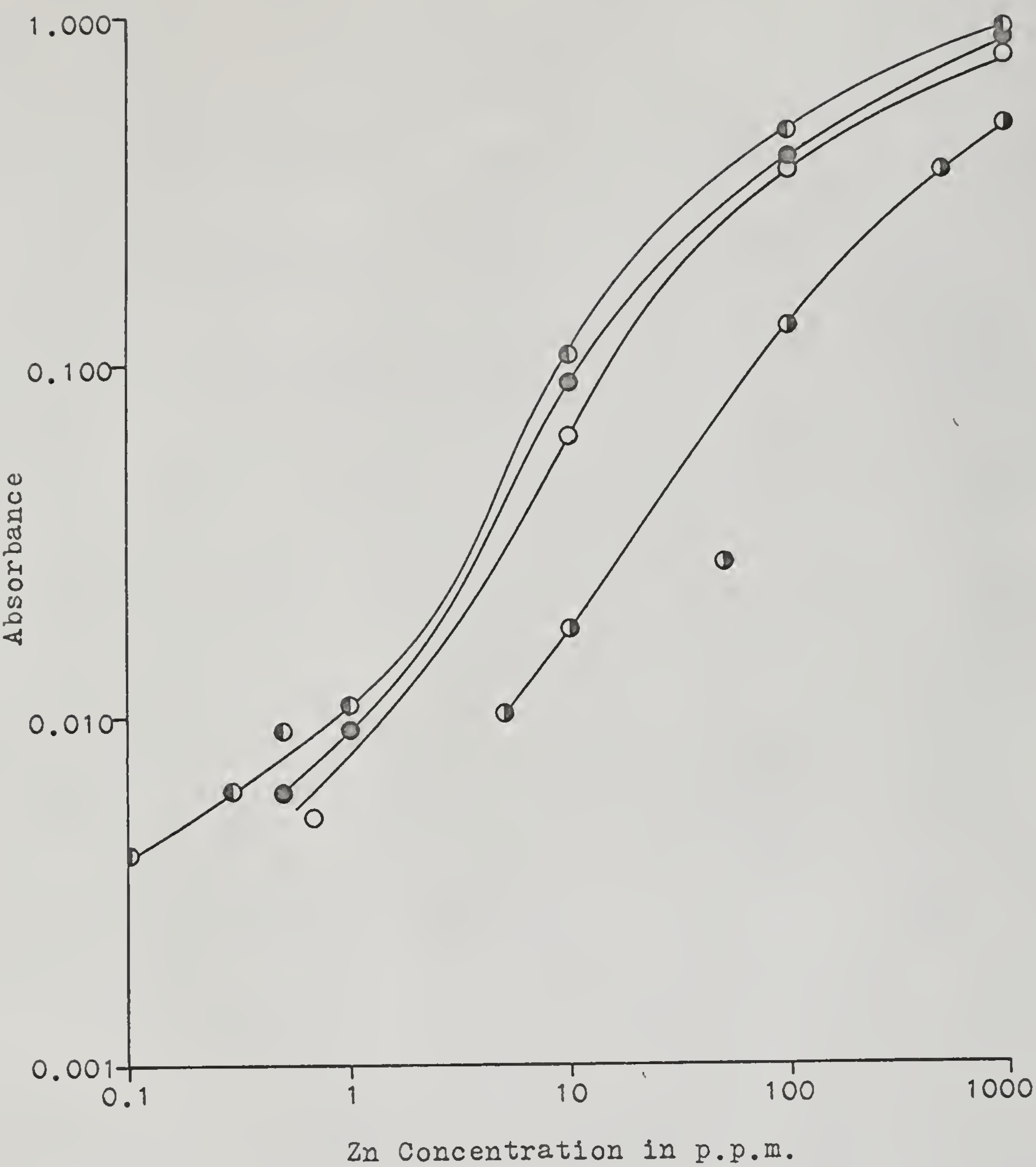

Figure 18. Atomic Absorption Working Curves for Zinc (Zn 2139 A. Line) Introduced into Different Flames

○	H_2/O_2
●	C_2H_2/O_2
◐	H_2/air
◑	Natural gas/air

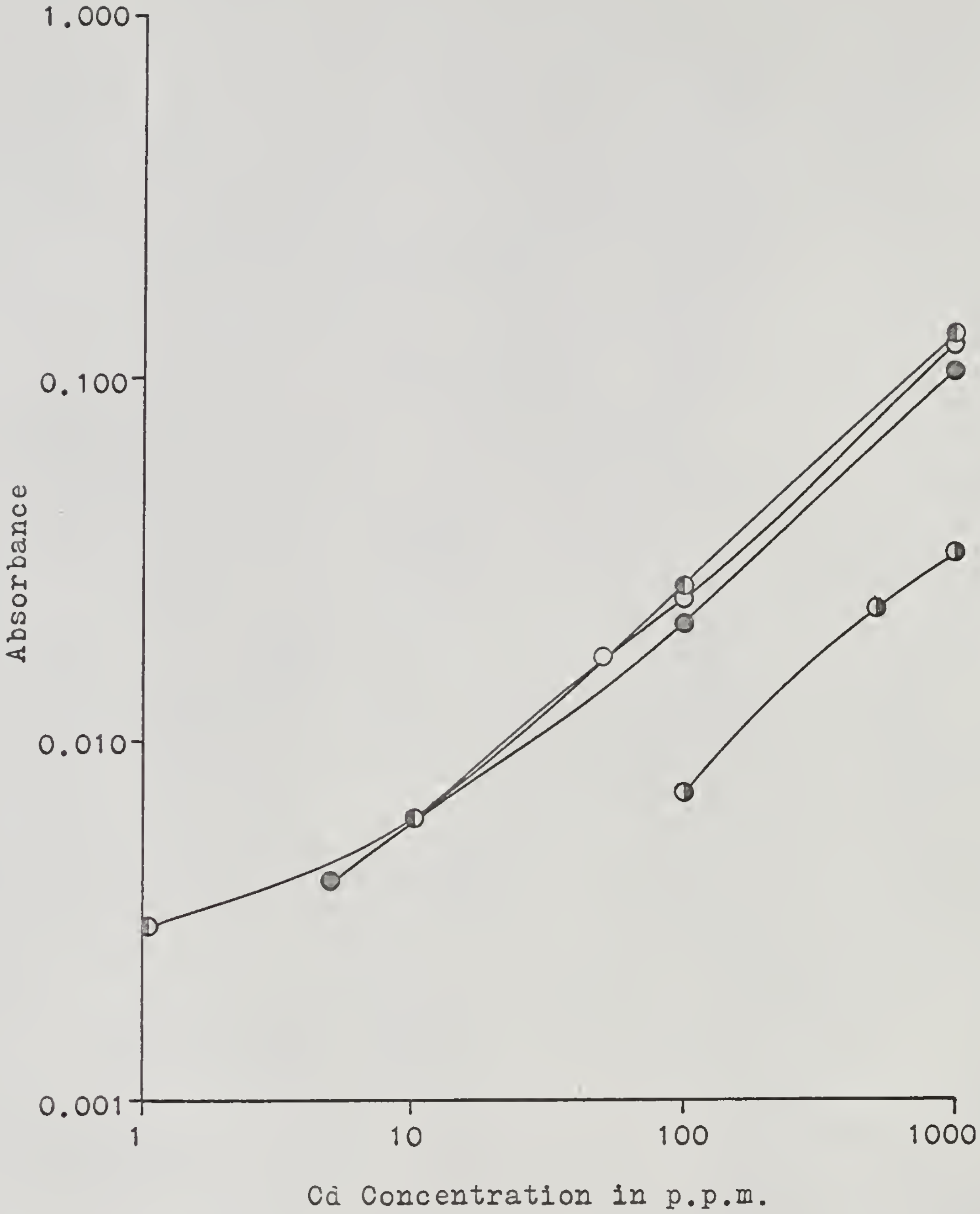

Figure 19. Atomic Absorption Working Curves for Cadmium (Cd 2288 A. Line) Introduced into Different Flames

○ H_2/O_2

● C_2H_2/O_2

◐ H_2/air

◑ Natural gas/air

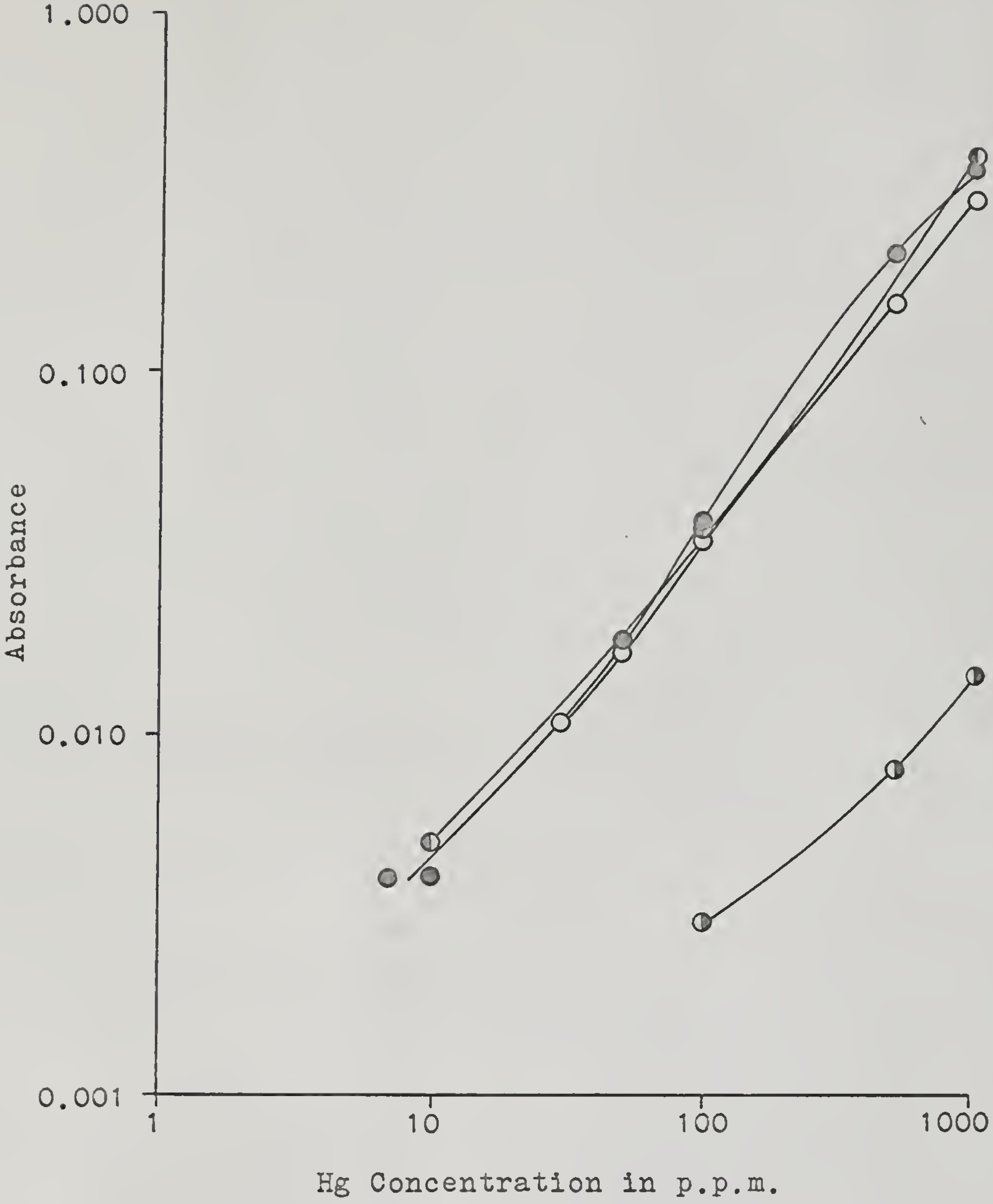

Figure 20. Atomic Absorption Working Curves for Mercury (Hg 2537 A. Line) Introduced into Different Flames Using the Electrodeless Discharge Tube

○	H_2/O_2
●	C_2H_2/O_2
◐	H_2/air
◑	Natural gas/air

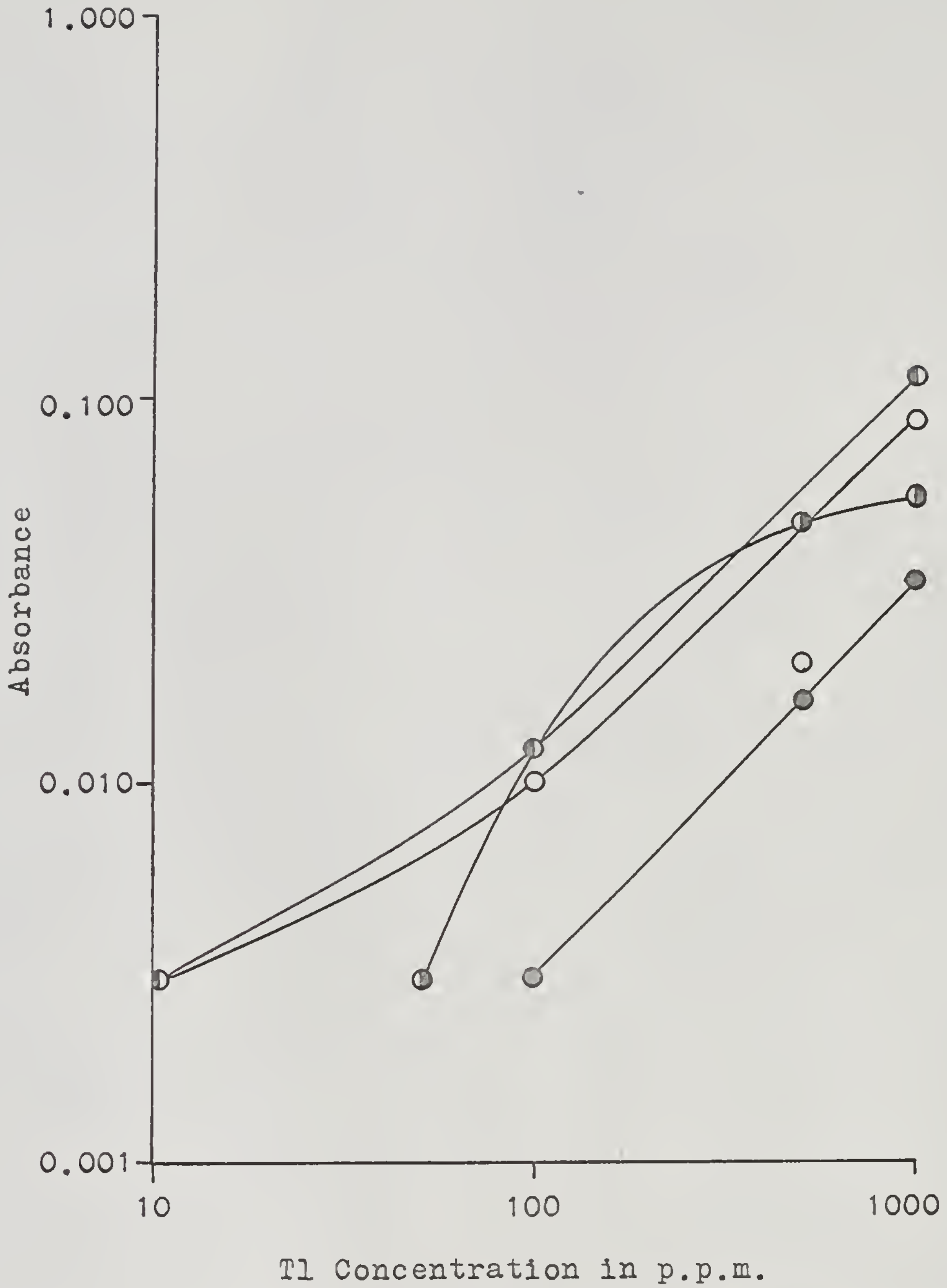

Figure 21. Atomic Absorption Working Curves for Thallium (Tl 3776 A. Line) Introduced into Different Flames

○ H_2/O_2

● C_2H_2/O_2

◐ H_2/air

◑ Natural gas/air

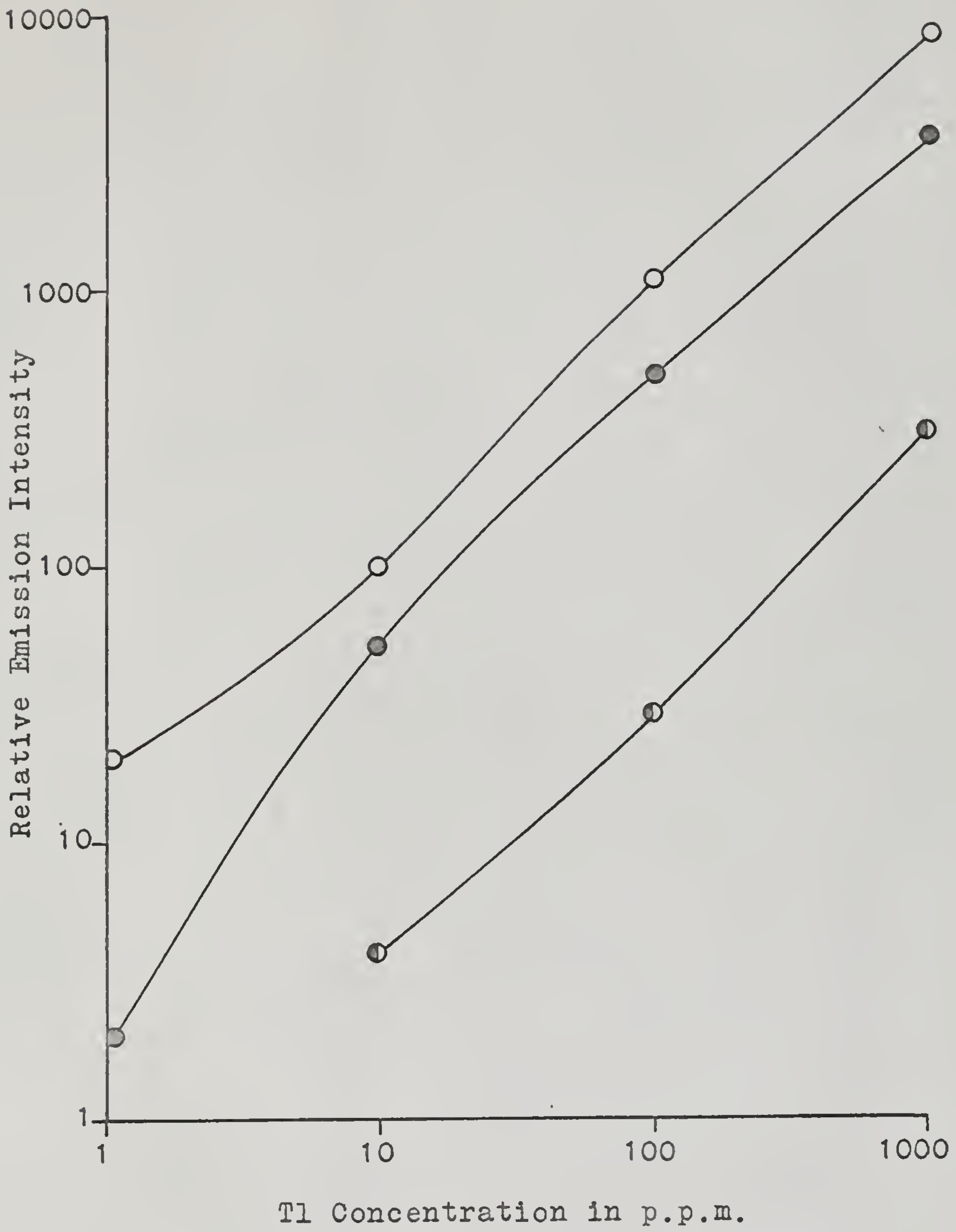

Figure 22. Atomic Emission Working Curves for Thallium (Tl 3776 A. Line) Introduced into Different Flames

○	H_2/O_2
●	C_2H_2/O_2
◐	H_2/air

APPENDIX B

TABLES OF ACCURACY AND SIGNAL-TO-NOISE RATIO

Key to Flame Abbreviations

Symbol	Flame
aN	Natural gas/air
aH	H_2/air
OH	H_2/O_2
OH*	Sheathed H_2/O_2
OA	C_2H_2/O_2

Key to Solvent Abbreviations

Symbol	Solvent
H_2O	Water
Me OH	Methanol

Table 8

Effect of Gases Added to Fuel Gas and Sheath, Percentage Standard Deviations, and Signal-to-Noise Ratios for Atomic Fluorescence Measurements of Zn 2139 Å.

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
aN	H_2O	None	1	85	3.4	48
			10	800	8.9	45
			100	4800	1.5	68
aH	H_2O	None	1	116	3.2	33
			10	657	1.7	74
			100	784	3.4	37
OH	H_2O	None	1	51	5.2	51
			10	395	1.5	65
			100	890	2.6	71
	30% MeOH		1	79	2.5	45
			10	537	1.0	62
			100	683	2.4	26
	70% MeOH		1	125	1.9	24
			10	580	1.4	37
			100	460	6.0	22
	H_2O	Ar	10	355	1.8	67
		N_2		359	3.0	51
	30% MeOH	Ar		408	1.5	58
		N_2		397	3.1	56
	70% MeOH	Ar		560	2.0	45
		N_2		538	1.4	51

Table 8 continued

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
OH^*	H_2O	Ar	10	445	1.6	83
		N_2		408	3.4	58
		O_2		407	3.6	46
	30% MeOH	Ar		520	2.1	24
		N_2		438	2.4	50
		O_2		475	3.5	67
	70% MeOH	Ar		630	3.9	15
		N_2		551	2.3	39
		O_2		585	0.8	55
OA	H_2O	None	1	45	5.2	11
			10	445	1.6	41
			100	710	2.6	48
	30% MeOH		1	96	5.0	27
			10	570	2.1	80
			100	742	2.1	83
	70% MeOH		1	145	2.7	20
			10	716	2.0	78
			100	697	4.2	27
	H_2O	Ar	10	505	2.3	85
		N_2		478	4.5	87
	30% MeOH	Ar		750	3.9	40
		N_2		660	3.2	36
	70% MeOH	Ar		955	3.7	48
		N_2		815	7.4	22

Table 9

Effect of Gases Added to Fuel Gas, Percentage Standard Deviations, and Signal-to-Noise Ratios for Atomic Fluorescence Measurements of Cd 2288 A.

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
aN	H_2O	None	1	6.5	12	9.2
			10	108	4.8	31
			100	810	3.6	23
aH	H_2O	None	1	20	22	3.8
			10	181	3.4	34
			100	434	1.8	49
OH	H_2O	None	1	11	11	4.8
			10	102	4.5	58
			100	328	4.2	60
	30% MeOH		1	17	27	3.4
			10	127	4.0	25
			100	392	1.6	76
	70% MeOH		1	23	20	9.1
			10	157	3.4	31
			100	435	3.5	42
	H_2O	Ar	10	96	8.7	19
		N_2		85	3.9	18
	30% MeOH	Ar		103	7.0	15
		N_2		99	6.7	32
	70% MeOH	Ar		152	2.4	29
		N_2		136	6.1	29

Table 9 continued

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
OA	H_2O	None	1	14	11	4.5
			10	89	4.5	16
			100	312	4.2	35
	30% MeOH		1	14	15	4.8
			10	87	4.5	20
			100	251	2.3	56
	70% MeOH		1	20	25	4.8
			10	123	4.5	29
			100	276	2.9	44
	H_2O	Ar	10	97	5.0	23
		N_2		93	1.9	24
	30% MeOH	Ar		106	4.2	17
		N_2		89	4.0	15
	70% MeOH	Ar		128	2.6	15
		N_2		108	6.3	14

Table 10

Effect of Gases Added to Fuel Gas and Sheath, Percentage Standard Deviations, and Signal-to-Noise Ratios for Atomic Fluorescence Measurements of Hg 2537 A.

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
aN	H_2O	None	10	3.8	25	3.6
			100	26	3.0	21
aH	H_2O	None	1	5.4	24	6.1
			10	69	1.7	65
			100	760	0.8	54
OH	H_2O	None	1	7.2	---	9.4
			10	36	4.2	35
			100	425	0.9	61
	30% MeOH		1	2.5	15	3.2
			10	27	3.2	28
			100	251	1.7	32
	70% MeOH		1	2.6	15	2.5
			10	34	3.2	28
			100	335	2.1	39
	H_2O	Ar	10	28	2.2	30
		N_2		28	1.9	26
	30% MeOH	Ar		23	3.2	24
		N_2		24	2.9	23
	70% MeOH	Ar		25	3.5	27
		N_2		28	3.0	26

Table 10 continued

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
OH*	H_2O	Ar	10	39	2.4	38
		N_2		38	2.7	32
		O_2		38	2.8	36
	30% MeOH	Ar		32	2.0	37
		N_2		29	1.4	29
		O_2		30	2.5	29
	70% MeOH	Ar		34	3.7	40
		N_2		33	3.4	33
		O_2		30	3.3	29
OA	H_2O	None	1	4.5	---	3.5
			10	35	3.9	29
			100	473	1.7	45
	30% MeOH		1	3	17	3.5
			10	28	4.7	28
			100	304	1.1	60
	70% MeOH		1	3.6	24	3.4
			10	43	3.1	22
			100	430	1.0	25
	H_2O	Ar	10	40	1.7	26
		N_2		40	2.1	34
	30% MeOH	Ar		37	1.8	28
		N_2		39	2.8	28
	70% MeOH	Ar		48	2.8	31
		N_2		51	2.2	26

Table 11

Effect of Gases Added to Fuel Gas, Percentage Standard Deviations, and Signal-to-Noise Ratios for Atomic Fluorescence Measurements of Tl 3776 Å.

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
aN	H_2O	None	10	5.8	14	5.5
			100	72	4.9	41
aH	H_2O	None	10	4.2	11.5	12
			100	35	2.1	28
			1000	277	2.3	26
OH	H_2O	None	10	1.7	9.6	7.1
			100	20.6	1.9	35
			1000	178	2.0	37
	30% MeOH		10	3.4	7.1	14
			100	37	3.1	20
	70% MeOH		10	13	---	7.8
			100	75	---	14
	H_2O	Ar	100	10.7	3.8	13
		N_2		12.5	5.2	13
	30% MeOH	Ar		16.7	1.8	20
		N_2		21.8	2.3	12
	70% MeOH	Ar		20.8	5.3	17
		N_2		21.9	3.3	13
OA	H_2O	None	10	1.2	27.3	2.4
			100	17.6	4.4	16
			1000	126	3.2	20

Table 11 continued

Flame	Solvent	Gas	Concentration in p.p.m.	I_F	% σ	S/N
OA	30% MeOH	None	10	1.5	24.9	4.2
			100	12.2	6.7	18
	70% MeOH		10	1.8	---	2.8
			100	18	---	14
	H_2O	Ar	100	19.5	5.9	15
		N_2		11.9	3.2	15
	30% MeOH	Ar		17.3	4.7	15
		N_2		9.5	0	12
	70% MeOH	Ar		20.5	3.6	19
		N_2		12.8	2.3	10

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BIOGRAPHICAL SKETCH

Robert Allan Staab was born July 11, 1937, at Chicago, Illinois. He received his elementary education in the public school system of Elmhurst, Illinois, and after moving to West Palm Beach, Florida, in January, 1953, he was graduated from Palm Beach High School in 1955. He has attended the University of Florida since September, 1955, and received the Bachelor of Science in Education degree in June, 1960, and the Master of Education degree in August, 1961. Since that time he has pursued his studies toward the degree, Doctor of Philosophy.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 18, 1964

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